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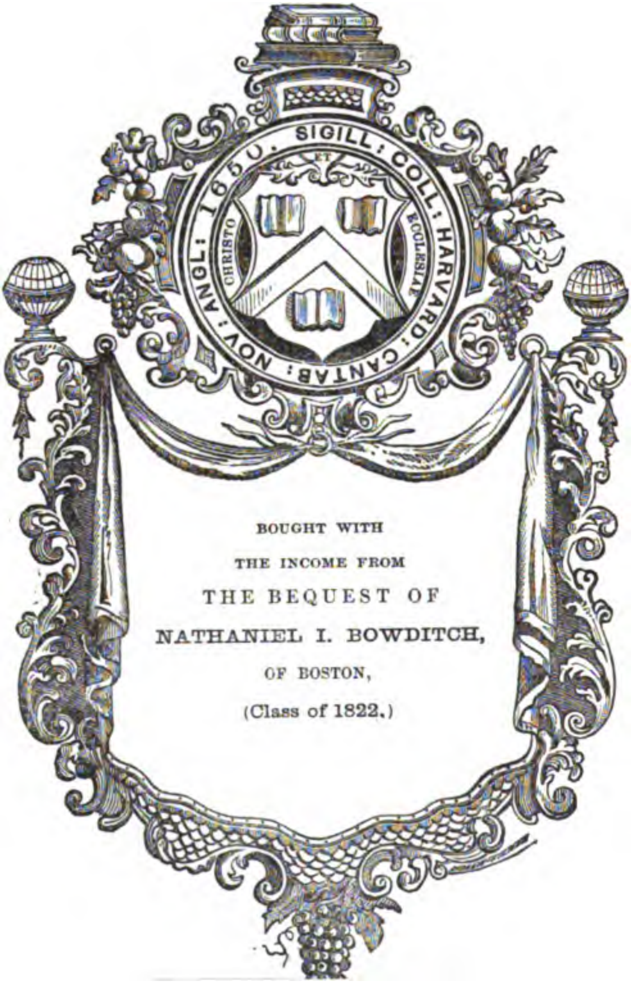

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A

THEORETICAL AND PRACTICAL TREATISE ON THE MANUFACTURE OF SULPHURIC ACID AND ALKALI, WITH THE COLLATERAL BRANCHES.

BY

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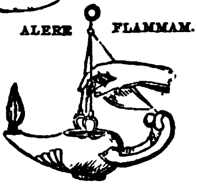
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PREFACE.

The present treatise is intended to supply various wants, and, accordingly, appeals to various classes of readers. In the first place, it gives a scientific description of all the substances occurring in the manufacture of sulphuric acid, alkali, and bleaching-powder, either as raw materials or finished products, according to the most recent statements, and thus saves the reader the trouble of collecting the latter for himself whenever he stands in need of them. Secondly, it is intended as an aid in the study of technical chemistry, by giving a complete description, both technical and theoretical, of all the processes occurring in this series of manufactures. Its third and principal object is to give to practical manufacturers both complete and reliable information upon all the apparatus and processes which have come under the author's notice, and thus to enable them to know what has been done in this field beyond the range of their own personal observation.

These objects, especially the third, could not be accomplished without treating the matter in question far more in detail and more in the style of a monograph than has been hitherto attempted. Much space is taken up by the discussion of the innumerable publications, in the English, German, and French languages, referring to this industry; but even more space was required for the faithful rendering of the author's personal observations and experiences. His own practice of eleven years in the North of England has been supplemented by numerous visits to the other alkali-manufacturing districts of Britain, and to those of Belgium, France, Germany, and Austria. The author's present position as Professor at a technical High School enables him to state frankly what he knows and what he has seen, since he can expect no benefit whatever from keeping any thing back. In his visits he has, of course, been favoured with some confidential communications, which he is not at liberty to reproduce here as he received them; but in every case he has obtained permission to make use of the *substance* of such communications for this treatise, and in the vast majority of cases no restraint whatever has been placed upon him. The author takes this opportunity of publicly thanking the many owners, managers, and chemists of alkali-works who have assisted him in his efforts to make this treatise a thoroughly practical and, above all, a trustworthy book of reference.

The British reader will in this book find the description of many apparatus and processes, and of a large number of facts, partly published abroad, partly never published as yet, but all of them comparatively or almost entirely unknown in his country. But this has not been done to the exclusion of the British styles of working and of the inventions made here, which, on the contrary, form the groundwork of the whole treatise, since the author's personal working experience was gained in England. But it would have ill suited his purpose if he had confined himself to describing his own experience, even when coupled with his notes of what he had observed on his visits elsewhere; he has ransacked the chemical and technical literature, and has not scrupled to mention nearly every thing, of course very briefly, which he has found bearing upon his subject. This seemed to be unavoidable; for under different circumstances the employment of different processes is not merely permissible, but frequently imperative. Even from decidedly antiquated processes the modern manufacturer may derive suggestions for fresh improvements. It was not very easy to marshal the enormous array of facts thus accumulated, without fatiguing the reader and enhancing the difficulty of studying the book; but the author has endeavoured to accomplish this task, by giving decided prominence to the processes now in general use, and grouping the others around them, appending critical remarks as to their practicability, wherever this was possible. It cannot be fairly expected that in all and every case he should have succeeded in discriminating the wheat from the chaff; some of the processes recommended by him may in the meantime have been replaced by better ones; there will be hardly any larger manufactory which does not in particular points exhibit some improvements upon the apparatus and processes as described here; but the author believes he is not mistaken in asserting that he has missed nothing of *importance,* and that, looking at the very large store of facts offered by him, even the most experienced manufacturer might derive valuable information from this treatise. Without this conviction the author would not dare to come before the public with a work pretentious by its very size.

The illustrations are very numerous, to a great extent from working-drawings, nearly all drawn to scale, and with such details that furnaces and other apparatus can be constructed from them without any further assistance. Many of these are obtained by the favour of some of the largest and best alkali-makers; and they are all the more valuable, as only the most approved forms of apparatus have been selected.

Whatever in this book is taken from previous publications is nearly always quoted, with chapter and section, or volume and page; so that the studious reader may verify it or pursue the subject further. The remainder, so far as it is not common property, is taken from the author's own observations, at the works formerly managed by himself or elsewhere. An appendix at the end of the second volume will embrace the publications appearing during the time this treatise is in the press, and additional information obtained by the author from private sources during the same time; and an exact reference-index will facilitate its use.

The Polytechnic School, Zürich,
April 1879.

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INTRODUCTION.

Among all branches of chemical industry the cycle of technical operations connected with alkali-making is preeminent, not merely from the magnitude of the works and the absolute bulk of the raw materials used and the quantity produced, but also from the fact that most other chemical products require one or more branches of alkali-making as the conditions of their own existence. We use the expression "alkali-making" in its widest sense, embracing the manufacture of sulphuric acid, sulphate of soda, muriatic acid, soda-ash, &c., and bleaching-powder; and we include in it also those works which do not complete the cycle, but stop, for instance, at sulphate of soda or even at sulphuric acid itself, since most factories making these as intermediate products are also sellers of them, and no strict separation can be made in this respect. In this wider meaning the products of alkali-making are necessary materials for many metallurgical processes, for the manufacture of artificial manures, soap, fatty and mineral oils, glass, paper, many inorganic and organic colouring-matters (especially nearly all coal-tar dyes), and even of many articles of food,—that is to say, for nearly all branches of manufacturing chemistry. It can be truly said that the manufacture of acids and alkali is the foundation upon which the whole chemical industry of our times is built up, and that such industry cannot be much developed in any country not possessing a flourishing alkali trade, or not being at least specially well situated for buying the produce of the latter. It is thus evident how great is the importance of the alkali trade in its wider meaning to the civilization of mankind, though we should certainly be going too far if we measured, as some have done, the civilization of a country by the development of this special industry.

The different branches of alkali-making mentioned above, to which may be added several by-products only obtained in certain works (such as copper, iron-oxide, regenerated sulphur, Epsom-salts, chlorate of potash, bicarbonate of soda, chloride of barium, &c.), are organically connected in such a manner that only under special local conditions can one or more of the principal substances be omitted. The initial process is nearly always the manufacture of *sulphuric acid* by burning brimstone or pyrites with the aid of nitrate of soda and of fuel, in many cases leaving a residue from which copper, iron-oxide, and even silver are obtained. The sulphuric acid then enters largely into manufactures not belonging to this cycle, of which only that of superphosphate is, as a rule, conducted on a sufficiently large scale to admit of the establishment of works for it exclusively. With this one very large and a few small exceptions, the manufacture of sulphuric acid is at once followed in the same works by a second step, viz. the manufacture of *sulphate of soda* by decomposing common salt with sulphuric acid, *muriatic acid* appearing as a by-product. Both articles are again required in several other chemical industries, and are accordingly sold as they are; but for the most part they only serve as intermediaries, the sulphate being further worked up to *soda-ash*, the muriatic acid to *bleaching-powder*, more rarely to *chlorate of potash*, at the same works. For these purposes, of course, new raw materials have to be introduced into the manufacturing cycle, of which we cannot as yet treat. Only this must be pointed out—why the cycle, whose principal members are sulphuric acid (vitriol), sulphate of soda, muriatic acid, and bleaching-powder, is mostly completed in one and the same factory, seeing that each of the first-mentioned products forms a raw material for many other chemicals besides soda-ash and bleaching-powder themselves. A principal reason for this is, that the two acids, sulphuric and muriatic, both from their liquid state and their extremely corrosive properties, require a very costly and at the same time fragile kind of packing which is also so bulky that the cost of transit of those acids for any great distance becomes very large*.

Naturally, therefore, those manufacturers who required sulphuric acid in very large quantities set to make it themselves, in order to save the cost of packing and carriage. Since sulphuric acid can only be made advantageously on a large scale, for some time sulphate of soda was the only article for which its own acid was made at the same works; and to this day this is the case at well-nigh all sulphate works. Only lately, and quite generally only in Great Britain, has the manufacture of superphosphates become so important that the establishment of vitriol-works for this exclusive purpose has become possible.

Some works stop at this stage; that is, they sell their sulphate of soda as such, either for the manufacture of glass &c. or to alkali works; especially is this the case in countries where fuel is too dear for making alkali with a profit. The calcined sulphate of soda, or saltcake, is a solid body, easily carried, not merely in ordinary casks, but loose, in whole truck- or ship-loads. On the other hand, the muriatic acid, which appears as an unavoidable by-product, is in the same predicament as vitriol; that is to say, the expense of packing and carriage forbids its sale in large quantities and conveyance to great distances. Very frequently (though certainly much more rarely now than formerly) the muriatic acid, liquefied solely for the sake of not laying waste the vegetation of the country around, was run into the nearest watercourse, whose water was any thing but improved by it. It was therefore a matter of importance to utilize the muriatic acid in a form in which the difficulties of transit were overcome; and, fortunately, such a form had been found, even before the development of the alkali-manufacture, in *bleaching-powder*. Probably all works not going beyond saltcake are compelled to utilize their muriatic acid in some way; and they do it mostly by the production of bleaching-powder, more rarely by that of chlorate of potash, of bicarbonate, or by using up liquid acid itself.

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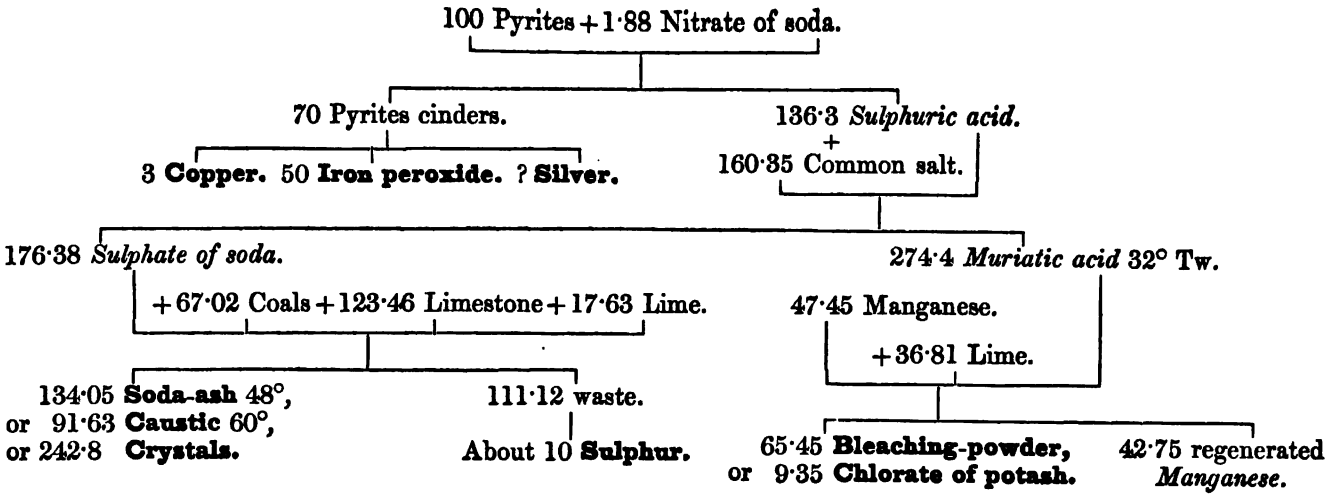
* In the case of sulphuric acid, the glass carboys have recently been partly superseded, as we shall see further on.

By far the largest quantity of sulphate of soda is used for making from it *soda-ash* (alkali) according to the method of Leblanc; and nothing, therefore, was more natural than that the alkali-works should produce their own saltcake, which necessarily led to manufacturing the vitriol required for the saltcake, and also, unless the muriatic acid could be sold or run to waste, to utilizing it in the way just described. Thus the chain on the whole was complete; for the further utilization of soda-ash is too multifarious, and the manufactures using it are on their part too complicated, for them to have been grafted upon alkali-making. The only important exception to this is the manufacture of soap, which certainly is frequently carried on as an accessory to alkali-making, but is not generally included in this term, and will not be described in this treatise.

The actual circumstances are in practice much more varied than those described here; but mostly they again lead to a combination of the branches of manufacture mentioned. Thus, for instance, there are works which make their best profit in selling muriatic acid, or the articles made with its aid. These must at least make their own vitriol and their sulphate of soda in order to obtain muriatic acid.

But since, in most cases, the sale of sulphate is restricted, and does not pay (owing to its cheapness) for carriage to long distances, except by water, the manufacturer ultimately is obliged to convert it into alkali, even if the selling-price of the alkali does not cover the expense of making it. The muriatic acid and the products made from it must then make good the deficiency, and leave a margin for profit besides.

The following Table will make the above clearer: it is principally taken from a paper of Mr. Mactear's ("On the Growth of the Alkali and Bleaching-powder Manufacture of the Glasgow District"); and it is hardly necessary to state that the figures contained in it are only valid for the St.-Rollox Works, and that the by-products are different in different works; the end-products and intermediate products are distinguished from the raw materials by variations in type :—


100 Pyrites + 1·88 Nitrate of soda.
70 Pyrites cinders.
136·3 *Sulphuric acid.* + 160·35 Common salt.
3 **Copper.** 50 **Iron peroxide.** ? **Silver.**
176·38 *Sulphate of soda.*
274·4 *Muriatic acid* 32° Tw.
+ 67·02 Coals + 123·46 Limestone + 17·63 Lime.
47·45 Manganese.
+ 36·81 Lime.
134·05 **Soda-ash** 48°,
or 91·63 **Caustic** 60°,
or 242·8 **Crystals.**
111·12 waste.
About 10 **Sulphur.**
65·45 **Bleaching-powder,**
or 9·35 **Chlorate of potash.**
42·75 regenerated *Manganese.*

FIRST BOOK.

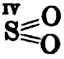
SULPHURIC ACID.

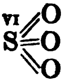
CHAPTER I.

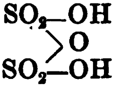
CHEMICAL AND PHYSICAL PROPERTIES OF THE OXIDES OF SULPHUR.

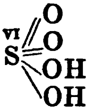
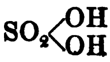
Sulphur gives the following compounds with oxygen, partly also with hydrogen, most of which have some importance in the manufacture of sulphuric acid or soda-ash :—

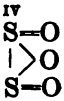
SO_2H_2 Hydrosulphurous acid .... $H\overset{IV}{S}O{-}OH$
(Hyposulphurous acid of Roscoe.)

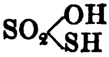
SO_2 Sulphur dioxide ....

(Sulphurous anhydride.)

SO_3 Sulphuric anhydride............


$S_2O_7H_2$ Pyrosulphuric acid


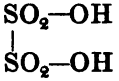
SO_4H_2 Sulphuric acid ....

or


S_2O_3 Sulphur sesquioxide ....


$S_2O_3H_2$ Hyposulphurous acid............

(Thiosulphuric acid.)

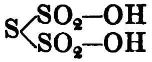
$S_2O_6H_2$ Dithionic acid ....

(Hyposulphuric acid.)



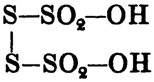
$$\begin{array}{l} SO_2-OH \\ \;| \\ SO_2-OH \end{array}$$

$S_3O_6H_2$ Trithionic acid ....



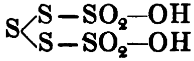
$$S\begin{array}{l} \diagup SO_2-OH \\ \diagdown SO_2-OH \end{array}$$

$S_4O_6H_2$ Tetrathionic acid ....



$$\begin{array}{l} S-SO_2-OH \\ | \\ S-SO_2-OH \end{array}$$

$S_5O_6H_2$ Pentathionic acid ....



$$S\begin{array}{l} \diagup S-SO_2-OH \\ \diagdown S-SO_2-OH \end{array}$$

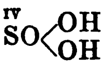
Only the second, third, and fourth compounds of this series are sufficiently important for our purpose to be described in detail (principally according to Gmelin-Krant's 'Handbuch der Chemie,' 6th edition, the newer literature being constantly consulted).

SULPHUR DIOXIDE, SO_2.

(Sulphurous Acid, Sulphurous Anhydride.)

Sulphur dioxide contains 50 parts by weight of sulphur and 50 parts of oxygen. It is a colourless gas of suffocating smell, neither combustible nor supporting combustion; in presence of water it exhibits pretty strongly acid properties, and at the same time exerts a bleaching action upon many organic colouring-matters. Vapour-density 2·21126 (air = 1). A litre of the gas weighs 2·86 grms. By cooling below −10° C., or by strong pressure at the ordinary temperature, it can be condensed to a liquid of the specific gravity 1·49 at −20° C., from which, by rapid evaporation, the solid compound can be obtained.

The compound SO_2 is only the anhydride; but it is very frequently called "sulphurous acid," the real hydrated acid (SO_3H_2) not being obtainable. This hypothetic acid, according to the properties of its salts, is represented by either of the following formulæ :—



$$\overset{IV}{S}O\begin{array}{l} \diagup OH \\ \diagdown OH \end{array} \quad \text{or} \quad H\overset{VI}{S}O_2-OH.$$

In any case both hydrogen atoms can be replaced by metals &c.

The oxide SO_2 is produced by burning brimstone, and by heating (roasting) many metallic sulphides, in the presence of air—by the action of strong mineral acids, both on its own salts, the sulphites, and on the hyposulphites (thiosulphates) and all polythionic acids—by heating sulphuric anhydride with brimstone, or by heating oil of vitriol with brimstone, coal, organic substances, or several metals—by strongly heating the vapour of sulphuric anhydride, or sulphuric acid, along with oxygen, and respectively water—and by igniting many sulphates, whereby the sulphuric anhydride first liberated at once splits up into sulphur dioxide and oxygen.

Thus sulphur dioxide is produced from sulphuric acid or anhydride (in many ways) by reductive processes. But, on the other hand, the sulphur dioxide passes over, even more easily, into sulphuric acid by oxidation processes; and it is accordingly one of the most frequent and potent reducing agents. Under certain conditions, by the action of light, of the electric current, or of a very high temperature and pressure combined, the sulphur dioxide splits up into sulphur and sulphuric anhydride. In the presence of oxygen (for instance, that of atmospheric air), or of bodies easily parting with their oxygen (such as the higher oxides of nitrogen, of manganese, of lead), sulphuric acid or its salts are formed. A very important reaction is that between SO_2 and sulphuretted hydrogen, H_2S. When completely dry, the two gases do not seem to act upon each other. Even in the presence of moisture no action takes place if the temperature is above 400° C. (E. Mulder). At the ordinary temperature water and sulphur are produced, but at the same time always pentathionic acid, according to the equation

$$5\,SO_2 + 5\,H_2S = S_5O_6H_2 + 4\,H_2O + 5\,S.$$

Probably there is simultaneously this action,

$$SO_2 + 2\,H_2S = 2\,H_2O + S_3,$$

according to the proportion of the two gases in the mixture.

With water sulphur dioxide does not form sulphurous acid proper, SO_3H_2, but only, under certain conditions, a solid compound with much more water (9, 11, or 15 H_2O to SO_2), which has not yet been definitively investigated. The sulphur dioxide dissolves pretty freely in water; and this solution behaves in every way as if it contained the real acid SO_3H_2; but constantly, even at the ordinary temperature, the dioxide (SO_2) evaporates from it. One volume of water absorbs, under 760 millims. pressure and at 0°, nearly 80 volumes SO_2. The coefficient of absorption, according to Bunsen and Schönfeld, at temperatures ranging between 0° and 20°, is

$$79{\cdot}789 - 2{\cdot}6077\,t + 0{\cdot}029349\,t^2;$$

at temperatures between 21° and 40°,

$$75{\cdot}182 - 2{\cdot}1716\,t + 0{\cdot}01903\,t^2.$$

The saturated acid contains at 0° 68·861 volumes of gaseous SO_2, and has a specific gravity of 1·06091; at 10° it contains 51·383 volumes gaseous SO_2, and has the spec. grav. 1·05472; at 20°, 36·206 volumes SO_2, spec. grav. 1·02386. The absorbed gas does not escape on freezing—and on boiling, only completely after a long time. Alcohol absorbs a much larger volume of sulphur dioxide (at 0° and 0·76 metre pressure, 328·62 volumes SO_2).

A table, not very much deviating from the above statements, of the solubility of sulphur dioxide in water at 0·76 metre mercurial pressure at different temperatures, is given in Kopp and Will's 'Jahresberichte' for 1861, p. 54.

Anthon's Table of the Densities of Solutions of Sulphurous Acid in Water (Jahresb. 1860, p. 694).

Specific gravity.	Per cent. SO_2.
1·005	0·95
1·009	1·90
1·013	2·86
1·016	3·82
1·020	4·77
1·023	5·72
1·027	6·68
1·031	7·63
1·036	8·59
1·046	9·54

Scott (Pharm. Soc. Journ. & Trans. xi. p. 217) gives the following Table of the solubility of aqueous sulphurous acid at 15° C. :—

Per cent. SO_2.	Specific gravity.
0·5	1·0028
1·0	1·0056
1·5	1·0085
2·0	1·0113
2·5	1·0141
3·0	1·0168
3·5	1·0194
4·0	1·0221
4·5	1·0248
5·0	1·0275
5·5	1·0302
6·0	1·0328
6·5	1·0353
7·0	1·0377
7·5	1·0401
8·0	1·0426
8·5	1·0450
9·0	1·0474
9·5	1·0497
10·0	1·0520

According to Scott, when making sulphurous acid (mixed with CO_2) by the process mostly used, viz. that of heating oil of vitriol with charcoal, the former is best employed with 74 per cent. $SO_3 = 165°$ Tw. If stronger vitriol be used, a portion of it is reduced to sulphur, which may give iron sulphide with the iron of the apparatus; with weaker acid sulphuretted hydrogen is formed. In order to obtain the gas as pure as possible, the washing-water should be mixed with lead sulphate or coarsely powdered charcoal.

According to its structural formula, sulphurous acid forms two series of salts—saturated or neutral ones, SO_3M_2, and acid ones, SO_3MH, isomorphous with the carbonates.

Sulphurous acid, apart from its production as the first step in the manufacture of sulphuric acid, serves for many other purposes, especially owing to its reducing, bleaching, and disinfecting action, which, however, do not concern us here. We must not, however, omit to state that it has an injurious action on both animal and vegetable organisms, especially the latter—different trees, shrubs, and plants being sensitive to it in very different degrees.

Sulphuric Anhydride, SO_3

(Sulphur Trioxide),

consists of 40 per cent. by weight of sulphur, and 60 per cent. of oxygen. According to Marignac and Schultz-Sellack, it exists in two different modifications, a liquid and a solid one. The liquid, α-anhydride melts at $+16°$ C., and begins to boil at $+35°$ (according to Schultz-Sellack, at 46°). Spec. grav. at $+13° = 1·9546$, at $+20°$

(melted) = 1·97. In the melted state it is less oily than oil of vitriol, and, if pure, colourless, but usually coloured brown by dust. When kept for some time at the ordinary temperature (below 25°) it is changed into the *solid*, β-anhydride, whose melting-point is stated very differently, from 50° to 100° C. Probably it begins to melt at 50°, and gradually passes over into the α-modification; it slowly evaporates even at the ordinary temperature. It forms fine, feathery, asbestos-like, white needles. The β-anhydride is perhaps a polymer of the α-modification. According to R. Weber, however (Poggendorff's Ann. clix. p. 313), the sulphur trioxide, obtained absolutely pure and free from water by his method, is at the summer temperature a very mobile, colourless liquid, which, on gradually cooling, solidifies to long, transparent, prismatic crystals similar to nitrate of potash, quite different from the white, opaque crystals of the ordinary anhydride containing a little water. These crystals melt at 14°·8 C. Under certain circumstances the anhydride can, like many other bodies, be cooled much below its proper melting-point without solidifying, but then solidifies suddenly. After a twelvemonth it still shows the same composition and the same melting-point as that which has been freshly prepared. Weber accordingly rejects the assumption of two different modifications, and ascribes the phenomena of this kind observed by others to a minimal residue of water.

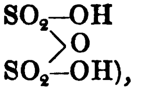
In moist air sulphuric anhydride at once forms dense white fumes; with water it hisses like a red-hot iron. Many organic substances are at once charred by it. In the complete absence of water it does not redden litmus. It gives several compounds with sulphur, whose colour, with the quantity of sulphur decreasing, changes from brown to green and blue. In the blue modification Weber has proved the presence of the sesquioxide, S_2O_3. With sulphur dioxide there seems to exist a distinct compound, $SO_2 + 2\,SO_3$. With water SO_3 at once combines to form sulphuric acid (SO_4H_2) and its different hydrates. It is, however, not easy to condense the sulphuric anhydride often produced in considerable quantity in technical processes *completely*, even with a large quantity of water and manifold contact; and quite special precautions have to be taken for this purpose.

The anhydride SO_3, when conducted through a red-hot tube, splits up into SO_2 and O, but is reformed from these gases at a somewhat lower heat, especially in the presence of platinum and several metallic oxides. We shall see the technical application of this reaction later on.

For scientific purposes the sulphuric anhydride is made by gently heating fuming oil of vitriol, or by igniting sodium pyrosulphate ($Na_2S_2O_7$). Its production in a perfectly pure state is described by Weber (*l. c.*). Almost up to the present time it has not been used for technical purposes, owing partly to the costliness of its production, partly to the supposed difficulty of handling and keeping it. Quite recently, however, its production has been made so much cheaper that certain branches of manufacture already employ it advantageously. Its keeping has turned out to be a very simple affair, as it can be sent out in drums made of tinned iron. Its handling is certainly unpleasant, since the contact of the skin with liquid anhydride, or even just liquefying by absorbing moisture, causes very malignant and slowly-curing burns. Its production on a manufacturing scale will be described in Chapter XVII.

PYROSULPHURIC ACID, $S_2O_7H_2$

(Structural formula,



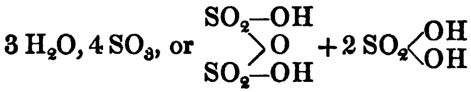
$$\begin{matrix} SO_2-OH \\ \rangle O \\ SO_2-OH \end{matrix}$$),

contains as constituents 89·89 parts of sulphuric anhydride and 10·11 of water, or equal molecules of hydrate and anhydride. A transparent crystalline mass, melting at 35° C., it decomposes at moderate heat into anhydride (SO_3) and oil of vitriol (SO_4H_2).

Pyrosulphuric acid is contained in the *Nordhausen fuming acid* of trade, which often consists altogether of it, and then bears the trade name, "solid oleum." Pyrosulphuric acid can also be easily obtained from the ordinary liquid fuming Nordhausen acid by cooling below 0°. Lastly, it can be made by carefully mixing anhydride with a small quantity of oil of vitriol. Weber (*l. c.*) obtained an intermediate hydrate, H_2SO_4, 3 SO_3, corresponding to 94·69 per cent. of SO_3.

Pyrosulphuric acid forms salts, of which those of the alkaline metals are the best-known and most important. Thus sodium pyrosulphate ($S_2O_7Na_2$) is formed by fusing acid sodium sulphate (SO_4NaH) at incipient red-heat (below 400° C.). At a full red-heat it splits up further into neutral sulphate (SO_4Na_2) and sulphuric anhydride (SO_3); this reaction is sometimes utilized for producing the latter compound. In contact with water, the pyrosulphates are gradually retransformed into acid sulphates.

A compound with 14·44 per cent. H_2O can also be obtained, which crystallizes in thin transparent prisms, fumes in the air, and melts at 26° C. Formula—



$$3\,H_2O, 4\,SO_3, \text{ or } \begin{matrix} SO_2-OH \\ \rangle O \\ SO_2-OH \end{matrix} + 2\,SO_2 \langle \begin{matrix} OH \\ OH \end{matrix}$$

The Nordhausen oil of vitriol, the manufacture of which will be described in the 17th Chapter, is a light-brown viscous oil of spec. grav. 1·896, representing a mixture of pyrosulphuric acid with sulphuric hydrate in varying proportions, and therefore solidifying at very different temperatures. It fumes in the air, and boils at 30° to 40° C., giving out vapours of anhydride, often 25 per cent. and upwards, whilst monohydrate remains behind. Water transforms it at once into ordinary oil of vitriol, with strong evolution of heat. It is nearly always coloured brown by organic substances, and, according to its mode of preparation, contains many other impurities, such as iron, sodium, calcium, aluminium, &c. (as sulphates), sulphurous acid, selenium, organic matters, &c. Since the receivers used in its preparation are charged with ordinary strong vitriol, the impurities of the latter will likewise pass into the fuming acid.

SULPHURIC ACID.

(Sulphuric Hydrate.)

Natural occurrence of Sulphuric Acid.

Owing to its strong affinity to all bases, sulphuric acid can only be found quite exceptionally in the free state in nature; whilst, on the other hand, the sulphates are found most extensively and sometimes in very great masses, especially gypsum and anhydrite, which form whole geological strata.

In the free state sulphuric acid has been found especially in a few springs of volcanic origin and in the rivers fed by those springs. One of the best-known cases of this kind is the Rio Vinagre or Pasambio, taking its origin from the volcano of Purace, a trachytic mountain whose top is covered by a layer of pure brimstone 18 inches deep, and which constantly sends forth gases and vapours. The name itself proves that the inhabitants of the surrounding country well knew its acid properties. Its water was examined first by Humboldt, then more exactly by Boussingault. The latter found in it 0·111 per cent. free sulphuric acid (calculated as SO_3) and 0·091 per cent. free hydrochloric acid, and calculated that this river daily carries into the sea about 38 tons of both acids. The Rio Vinagre takes its origin 11,600 feet above the level of the sea, and joins the river Cauca, into which, according to other statements ('Cosmos,' July 1869), it is said to empty daily 34,784 cubic metres of water containing 37,611 kilog. of sulphuric acid and 31,654 kilog. of hydrochloric acid. A still richer source exists in the Paramo de Ruiz, a volcano in New Granada: it was discovered by Degenfeldt and examined by Lewy, who found in it 0·5181 per cent. free sulphuric acid (SO_3) and 0·085 free hydrochloric acid.

Other waters of this kind are found at Byrontown in the State of Tennessee, in the lake of the extinct volcano Mount Indian in Java, at Aix in Savoy, in a grotto of Mount Zoccolino in Italy, in the neighbourhood of Siena, in the mud of the volcanos of Guatemala and San Salvador, in the sea-water at Santorin (where, according to Landerer, the copper oxide on the ships' sheathing is dissolved by it), and in the hot springs near the sulphur-beds at Krisank in Iceland. According to J. W. Mallet ('Chem. News,' xxvi. 147), similar acid waters occur in the Gulf of Mexico, not far from the mouth of the river Neches, and at other places in Louisiana, in one case containing 5·290 grms. $SO_6 H_2$ per litre. During the blockade of the Confederate ports in the American war of 1861 to 1864 the galvanic batteries of the telegraph stations in Texas and West Louisiana are said to have been supplied with this natural vitriol.

Boussingault ascribes the origin of such volcanic sulphuric acids to the action of hydrochloric acid on red-hot sulphates; the muriatic acid itself is generated by the action of chlorides and aqueous vapour on trachytic silicates. Such natural sulphuric acid is in any case also formed by the oxidation of pyrites and other sulphur ores, the acid being expelled by heat from the sulphates generated at first. Miners are only too familiar with the occurrence of free acid in pit-waters from similar causes, by the corrosion of metal pumps and steam-boilers; even the leather of the valves thereby becomes brittle, and the wooden parts are charred. In the case of volcanos, sulphuric acid will be formed by the oxidation of the sulphuretted hydrogen and the sulphurous acid from the fumaroles and solfataras.

41

Even in the animal kingdom free sulphuric acid has been found, viz. in the salivary glands of several mollusks, especially of *Dolium galea,* which contain 2·47 per cent. free sulphuric acid and 0·4 per cent. of free hydrochloric acid (Boedeker and Troschel; De Luca and Pauceri).

SULPHURIC ACID, ORDINARY OIL OF VITRIOL &c.

The proper sulphuric hydrate, $SO_4 H_2$ or $SO_2{<}\genfrac{}{}{0pt}{}{OH}{OH}$, is a limpid oily liquid of 1·854 sp. gr. at 0° C. (Marignac) or 1·857 (Kolb), 1·842 at 12°, 1·834 at 24° C. It solidifies at a low temperature to crystals, which melt at +10°·5 C., but generally show the phenomenon of superfusion; that is to say, they remain liquid a good deal below the above temperature, but the liquid mass solidifies directly as soon as a crystal of the solid hydrate is introduced into it. It does not fume at the ordinary temperature, but on heating to 30° or 40° C., when its dissociation into water and anhydride begins. The acid begins to boil at 290°; but it does not distil unchanged, a mixture of hydrated acid, anhydride, and water passing over; the boiling-point rises up to 338° C. (Marignac), and then remains constant.

The pure monohydrate has the formula $SO_4 H_2$, and is composed of

Sulphur	32	32·653
Oxygen	64	65·306
Hydrogen	2	2·041
	98	100·000

or

Anhydride	SO_3	81·63
Water	H_2O	18·37
		100·00

Accordingly it cannot be obtained by concentrating or distilling dilute acid, but only by the addition of an exactly sufficient quantity of anhydride to the acid about to be described, or by expelling the anhydride from fuming oil of vitriol by means of a dry current of air, or by cooling oil of vitriol below 0°. The real sulphuric hydrate is therefore only a scientific curiosity, and without any technical importance.

The strongest oil of vitriol obtainable by concentrating ordinary pure sulphuric acid contains a quantity of water which is not stated alike by different exact observers (Marignac, Pfaundler, Roscoe, Dittmar); so that it cannot be asserted that this acid constitutes a compound of monohydrate with water. The statements differ from 97·86 to 98·99 per cent. of $SO_4 H_2$ in this acid. This *distilled sulphuric acid* solidifies a little below 0°; but it also shows the phenomenon of superfusion in a very high degree. Its boiling-point is stated by Dalton to be 326° to 327° C.; by Marignac, 338°; by Pfaundler and Pölt, 315° to 317° C. Usually Marignac's statement is considered the most reliable; the acid of Pfaundler and Pölt probably contained a little more water. The boiling takes place quietly under a stronger pressure than the ordinary one, but at a lower pressure with violent bumping, which can be avoided by putting in platinum wire or scraps, according to Dittmar even better by conducting a slow current of air through it during the boiling (see Chapter XII., purification of sulphuric acid).

The *vapour* of sulphuric acid in any case consists for the most part, or even entirely (according to the temperature), not of the molecules $SO_4 H_2$, but of isolated molecules of SO_3 and $H_2 O$; theory would give to $SO_4 H_2$ (2 vols.) a vapour-density of 3·3862, for separated molecules of SO_3 and $H_2 O$ (4 vols.) a vapour-density of 1·6931, whilst Deville and Troost at 440° found it actually $=1·74$. The dissociation is therefore as good as complete in the state of vapour; and the assumption agrees very well with our present notions about the state of vapour (since Clausius), that also below the boiling-point a few molecules of SO_4H_2 are already formed, from which all the above-described phenomena are easily explained (Dittmar, 'Chem. News,' xx. 258).

The ordinary English oil of vitriol, such as is made in the platinum stills of the factories, apart from its other impurities, always contains a little more water than the distilled oil of vitriol. The ordinary acid of 170° Tw. (most of the acid, so-called, of 170° Tw. would only show 166° or even less with a properly graduated hydrometer) contains about 93 to 94 per cent. of monohydrate and 6 to 7 per cent. of water,—which cannot be made to square with certain atomic proportions; the sesquihydrate, $2\ SO_4 H_2 + H_2 O$, would contain 8·41 per cent. of water—that is, rather more than the ordinary strong vitriol. It is difficult to state any thing very certain on this point, since the hydrometers are not accurate enough for such high percentages, and since a very small difference in their indications answers to a considerable difference in the percentage of water in the acid. Baumé's hydrometers, which are those almost universally used on the continent, and 66° of which ought to correspond to the strongest oil of vitriol, are often made by immersing them in commercial vitriol, and putting the figure 66° to the point thus reached; such hydrometers are, of course, useless for accurate work. For technical purposes it is mostly sufficient to assume that the ordinary strong vitriol is equivalent to the sesquihydrate, $2\,SO_4\,H_2+H_2\,O$, which corresponds to a molecular weight of 214, or to an equivalent weight (for each hydroxyl) of 53·5, and to a percentage of 8·41 water; according to Bineau's table, acid of 1·843 at 0° or 1·830 at 15° C. will almost exactly answer to this. Such an acid shows 65½° with the rational Baumé's hydrometer, at 15°; but the hydrometers used at the factories usually show ½° in excess of this.

The only rational hydrometer on Baumé's system, resting on a mathematical basis, and therefore always obtainable in a uniform manner, is that graduated according to the formula

$$d=\frac{144{\cdot}3}{144{\cdot}3-n},$$

which is deduced as follows (Hofmann's 'Official Report on the Vienna Exhibition,' 1875, i. p. 180):—

If a hydrometer sinks in water up to 0°, and in a second liquid D of the density d only up to n°, the two unequal volumes of liquid displaced must have the same weight, viz. that of the hydrometer. If the latter weight is called G (taking as a unit the weight of a volume of water corresponding to the volume of one degree of the scale), we have

The weight of the volume of water displaced by the hydrometer......................................=	G
The weight of an equal volume of the liquid D, with a density $=d$	Gd
The weight of the water displaced by n degrees of the scale..	n
The weight of an equal volume of the liquid D	nd

Now it is evidently the latter weight by which the two weights Gd and G differ; and we have accordingly

$$Gd-G=nd,$$

from which follows

$$d=\frac{G}{G-n} \text{ and } G=\frac{nd}{d-1}.$$

For the case of sulphuric monohydrate of the density of 1·842 at 15° C., in which Baumé's hydrometer is to sink down to 66°, the value of G, by substituting the above values for d and n in the last equation is found =144·3, and accordingly

$$d=\frac{144{\cdot}3}{144{\cdot}3-n}.$$

The figure 144·3 appearing in this equation is the weight of the hydrometer, if the weight of a volume of water corresponding to the volume of one degree of the scale be taken as unit. The so-called Dutch hydrometer is constructed from a formula very closely approaching the above, viz.

$$d=\frac{144}{144-n};$$

and its figures accordingly deviate so little from those of the rational hydrometers, that we need take no further account of it; the degree 66° in this case answers to the specific gravity 1·847, against 1·842 of our "rational" hydrometer. The original Baumé's hydrometer was not made according to a formula, but in this way:—The instrument was first immersed in pure water and then in a ten-per-cent. solution of pure common salt in water (whose spec. grav., according to Gerlach, at 14° R. is =1·073110); the space between these two points was then divided into 10 equal degrees, which were continued upwards. According to Gerlach (Dingl. Journ. cxcviii. 315) the formula

$$\frac{100}{100-(0{\cdot}6813\times n)}=d$$

can be deduced from this, and the degree 66° on such a hydrometer is only =1·81706 spec. grav., which, according to Bineau and Kolb's table, is only =65° on the proper hydrometer (see below). This confusion is very much to be regretted; but in order to lessen it, we shall here tabulate the degrees of Baumé's hydrometer according to Gerlach, those according to the above rational formula (according to Kolb), and those according to Twaddle's hydrometer; the different columns show the specific gravity corresponding for each hydrometer to the degree of the first column placed opposite to it.

Degrees.	Baumé's Hydrometer (Gerlach).	Rational Hydrometer, $d=\frac{144\cdot3}{144\cdot3-n}$.	Twaddle's Hydrometer.	Degrees.	Baumé's Hydrometer (Gerlach).
1	1·0068	1·007	1·005	44	1·4281
2	1·0138	1·014	1·010	45	1·4421
3	1·0208	1·022	1·015	46	1·4564
4	1·0280	1·029	1·020	47	1·4710
5	1·0353	1·037	1·025	48	1·4860
6	1·0426	1·045	1·030	49	1·5012
7	1·0501	1·052	1·035	50	1·5167
8	1·0576	1·060	1·040	51	1·5325
9	1·0653	1·067	1·045	52	1·5487
10	1·0731	1·075	1·050	53	1·5652
11	1·0810	1·083	1·055	54	1·5820
12	1·0890	1·091	1·060	55	1·5993
13	1·0972	1·100	1·065	56	1·6169
14	1·1054	1·108	1·070	57	1·6349
15	1·1138	1·116	1·075	58	1·6533
16	1·1224	1·125	1·080	59	1·6721
17	1·1310	1·134	1·085	60	1·6914
18	1·1398	1·142	1·090	61	1·7111
19	1·1487	1·152	1·095	62	1·7313
20	1·1578	1·162	1·100	63	1·7520
21	1·1670	1·171	1·105	64	1·7731
22	1·1763	1·180	1·110	65	1·7948
23	1·1858	1·190	1·115	66	1·8171
24	1·1955	1·200	1·120	67	1·8398
25	1·2053	1·210	1·125	68	1·8632
26	1·2153	1·220	1·130	69	1·8871
27	1·2254	1·231	1·135	70	1·9117
28	1·2357	1·241	1·140	71	1·9370
29	1·2462	1·252	1·145	72	1·9629
30	1·2569	1·263	1·150	73	1·9895
31	1·2677	1·274	1·155	74	2·0167
32	1·2788	1·285	1·160	75	2·0449
33	1·2901	1·297	1·165	76	......
34	1·3015	1·308	1·170	77	......
35	1·3131	1·320	1·175	78	......
36	1·3250	1·332	1·180	79	......
37	1·3370	1·345	1·185	80	......
38	1·3494	1·357	1·190	81	......
39	1·3619	1·370	1·195	82	......
40	1·3746	1·383	1·200	83	......
41	1·3876	1·397	1·205	84	......
42	1·4009	1·410	1·210	85	......
43	1·4143	1·424	1·215	86	......

Rational Hydrometer, $d=\frac{144\cdot3}{144\cdot3-n}$.	Twaddle's Hydrometer.	Degrees.	Twaddle's Hydrometer.	Degrees.	Twaddle's Hydrometer.
1·438	1·220	87	1·435	130	1·650
1·453	1·225	88	1·440	131	1·655
1·468	1·230	89	1·445	132	1·660
1·483	1·235	90	1·450	133	1·665
1·498	1·240	91	1·455	134	1·670
1·514	1·245	92	1·460	135	1·675
1·530	1·250	93	1·465	136	1·680
1·540	1·255	94	1·470	137	1·685
1·563	1·260	95	1·475	138	1·690
1·580	1·265	96	1·480	139	1·695
1·597	1·270	97	1·485	140	1·700
1·615	1·275	98	1·490	141	1·705
1·634	1·280	99	1·495	142	1·710
1·652	1·285	100	1·500	143	1·715
1·671	1·290	101	1·505	144	1·720
1·691	1·295	102	1·510	145	1·725
1·711	1·300	103	1·515	146	1·730
1·732	1·305	104	1·520	147	1·735
1·753	1·310	105	1·525	148	1·740
1·774	1·315	106	1·530	149	1·745
1·796	1·320	107	1·535	150	1·750
1·819	1·325	108	1·540	151	1·755
1·842	1·330	109	1·545	152	1·760
......	1·335	110	1·550	153	1·765
......	1·340	111	1·555	154	1·770
......	1·345	112	1·560	155	1·775
......	1·350	113	1·565	156	1·780
......	1·355	114	1·570	157	1·785
......	1·360	115	1·575	158	1·790
......	1·365	116	1·580	159	1·795
......	1·370	117	1·585	160	1·800
......	1·375	118	1·590	161	1·805
......	1·380	119	1·595	162	1·810
......	1·385	120	1·600	163	1·815
......	1·390	121	1·605	164	1·820
......	1·395	122	1·610	165	1·825
......	1·400	123	1·615	166	1·830
......	1·405	124	1·620	167	1·835
......	1·410	125	1·625	168	1·840
......	1·415	126	1·630	169	1·845
......	1·420	127	1·635	170	1·850
......	1·425	128	1·640		
	1·430	129	1·645		

Whilst a sesquihydrate of sulphuric acid cannot be established as a certain chemical compound, the *double hydrate,* $SO_4H_2 + H_2O$, is known with certainty. It crystallizes from rather more dilute acid, for instance, acid of 144° Tw. in the cold. It contains 84·48 monohydrate +15·52 water (or 68·97 anhydride +31·03 water), melts at +8° C., but, owing to superfusion, generally only solidifies below this temperature (for instance, in the depth of winter); at 205° to 210° C. it already loses 1 mol. H_2O, and leaves ordinary oil of vitriol behind. The crystals form large clear hexagonal columns with six-pointed end-faces. Spec. grav. 1·78 to 1·79. By the crystallization of this hydrate carboys are often cracked in winter; acid of 144° Tw. and the like ought therefore only to be warehoused in places where the temperature will not sink too low—for instance, below the acid-chambers. Stronger or weaker acid can be exposed to the cold of winter without any danger.

Sometimes, according to Ure, a third hydrate, $SO_4H_2 + 2\,H_2O$, is assumed, because, on diluting strong vitriol with water down to this point (that is, corresponding to 73·13 per cent. monohydrate, or 59·70 per cent. of anhydride), the largest contraction, viz. from 100 volumes to 92·14 volumes, takes place. Bourgoin (Bull. Soc. Chem. [2] xii. 433) infers the same from observations on electrolyzing dilute vitriol. The density of this mixture is stated differently by different observers:—by Graham, at 1·6321; by Bineau, 1·665; by Kolb, 1·652; by Jacquelain, 1·6746. According to Liebig it boils at 163° to 170°; between 193° and 199° it loses one molecule of water, and is changed into $SO_4H_2 + H_2O$ (Graham).

The percentage of real acid in dilute sulphuric acid is mostly ascertained by its specific gravity, and this mostly by the hydrometer. The statements of different observers on this point certainly differ very much, even taking into account the temperature and the uncertainty in the relation between Baumé's degrees and the specific gravity. In the following the older tables of Vauquelin, Darcet, Dalton, Ure, &c. are neglected; only that of Bineau, which is most in use, and the newest one, that of Kolb (Bull. de la Soc. Industr. de Mulhouse, 1872, pp. 209, 238), are given, as well as the very useful accessory tables furnished by Kolb.

Bineau's Table of the percentage of Hydrate and Anhydride in Aqueous Sulphuric Acid.

Degrees (Baumé).	Spec. gravity.	At 0° C., per cent. of		At 15° C., per cent. of	
		Hydrate, SO_4H_2.	Anhydride, SO_3.	Hydrate, SO_4H_2.	Anhydride, SO_3.
5	1·036	5·1	4·2	5·4	4·5
10	1·075	10·3	8·4	10·9	8·9
15	1·116	15·5	12·7	16·3	13·3
20	1·161	21·2	17·3	22·4	18·3
25	1·209	27·2	22·2	28·3	23·1
30	1·262	33·6	27·4	34·8	28·4
33	1·296	37·6	30·7	38·9	31·8
35	1·320	40·4	33·0	41·6	34·0
36	1·332	41·7	34·1	43·0	35·1
37	1·345	43·1	35·2	44·3	36·2
38	1·357	44·5	36·3	45·5	37·2
39	1·370	45·9	37·5	46·9	38·3
40	1·383	47·3	38·6	48·4	39·5
41	1·397	48·7	39·7	49·9	40·7
42	1·410	50·0	40·8	51·2	41·8
43	1·424	51·4	41·9	52·5	42·9
44	1·438	52·8	43·1	54·0	44·1
45	1·453	54·3	44·3	55·4	45·2
46	1·468	55·7	45·5	56·9	46·4
47	1·483	57·1	46·6	58·2	47·5
48	1·498	58·5	47·8	59·6	48·7
49	1·514	60·0	49·0	61·1	50·0
50	1·530	61·4	50·1	62·6	51·1
51	1·546	62·9	51·3	63·9	52·2
52	1·563	64·4	52·6	65·4	53·4
53	1·580	65·9	53·8	66·9	54·6
54	1·597	67·4	55·0	68·4	55·8
55	1·615	68·9	56·2	70·0	57·1
56	1·634	70·5	57·5	71·6	58·4
57	1·652	72·1	58·8	73·2	59·7
58	1·671	73·6	60·1	74·7	61·0
59	1·691	75·2	61·4	76·3	62·3
60	1·711	76·9	62·8	78·0	63·6
61	1·732	78·6	64·2	79·8	65·1
62	1·753	80·4	65·7	81·7	66·7
63	1·774	82·4	67·2	83·9	68·5
64	1·796	84·6	69·0	86·3	70·4
65	1·819	87·4	71·3	89·5	73·0
65·5	1·830	89·1	72·7	91·8	74·9
65·8	1·837	90·4	73·8	94·5	77·1
66	1·842	91·3	74·5	100·0	81·6
66·2	1·846	92·5	75·5		
66·4	1·852	95·0	77·5		
66·6	1·857	100·0	81·6		

The specific gravities found at a temperature t° C. can, according to Bineau, be reduced to a temperature of 0° by multiplying with $\frac{144\cdot38}{144\cdot38-t}$; or the following Table can be used for correction:—

Specific gravity of the acid at 0°.	Decrease of specific gravity by a rise of 10° C. in temperature, or increase by a fall of 10° C.
1·04	0·002
1·07	0·003
1·10	0·004
1·15	0·005
1·20	0·006
1·30	0·007
1·45	0·008
1·70	0·009
1·85	0·0096

On mixing sulphuric acid and water a certain contraction takes place, so that the volume of the mixture is rather less than that of its two constituents. This matter has been treated in detail by Karmarsch ('Dingler's Journal,' ccxxvi. 449).

Kolb's Table of the percentage of real acid in aqueous sulphuric acid at 15° *C.'*

Degrees (Baumé).	Spec. grav.	100 parts by weight contain				1 litre contains in kilograms			
		SO_3.	SO_4H_2.	Acid of 60° Baumé	Acid of 53° Baumé	SO_3.	SO_4H_2.	Acid of 60° Baumé	Acid of 53° Baumé
0	1·000	0·7	0·9	1·2	1·3	0·007	0·009	0·012	0·013
1	1·007	1·5	1·9	2·4	2·8	0·015	0·019	0·024	0·028
2	1·014	2·3	2·8	3·6	4·2	0·023	0·028	0·036	0·042
3	1·022	3·1	3·8	4·9	5·7	0·032	0·039	0·050	0·058
4	1·029	3·9	4·8	6·1	7·2	0·040	0·049	0·063	0·074
5	1·037	4·7	5·8	7·4	8·7	0·049	0·060	0·077	0·090
6	1·045	5·6	6·8	8·7	10·2	0·059	0·071	0·091	0·107
7	1·052	6·4	7·8	10·0	11·7	0·067	0·082	0·105	0·123
8	1·060	7·2	8·8	11·3	13·1	0·076	0·093	0·120	0·139
9	1·067	8·0	9·8	12·6	14·6	0·085	0·105	0·134	0·156
10	1·075	8·8	10·8	13·8	16·1	0·095	0·116	0·148	0·173
11	1·083	9·7	11·9	15·2	17·8	0·105	0·129	0·165	0·193
12	1·091	10·6	13·0	16·7	19·4	0·116	0·142	0·182	0·211
13	1·100	11·5	14·1	18·1	21·0	0·126	0·155	0·199	0·231
14	1·108	12·4	15·2	19·5	22·7	0·137	0·168	0·216	0·251
15	1·116	13·2	16·2	20·7	24·2	0·147	0·181	0·231	0·270

Kolb's Table (continued).

Degrees (Baumé).	Spec. grav.	100 parts by weight contain				1 litre contains in kilograms			
		SO_3.	SO_4H_2.	Acid of 60° Baumé	Acid of 53° Baumé	SO_3.	SO_4H_2.	Acid of 60° Baumé	Acid of 53° Baumé
16	1·125	14·1	17·3	22·2	25·8	0·159	0·195	0·250	0·290
17	1·134	15·1	18·5	23·7	27·6	0·172	0·210	0·269	0·313
18	1·142	16·0	19·6	25·1	29·2	0·183	0·224	0·287	0·333
19	1·152	17·0	20·8	26·6	31·0	0·196	0·239	0·306	0·357
20	1·162	18·0	22·2	28·4	33·1	0·209	0·258	0·330	0·385
21	1·171	19·0	23·3	29·8	34·8	0·222	0·273	0·349	0·407
22	1·180	20·0	24·5	31·4	36·6	0·236	0·289	0·370	0·432
23	1·190	21·1	25·8	33·0	38·5	0·251	0·307	0·393	0·458
24	1·200	22·1	27·1	34·7	40·5	0·265	0·325	0·416	0·486
25	1·210	23·2	28·4	36·4	42·4	0·281	0·344	0·440	0·513
26	1·220	24·2	29·6	37·9	44·2	0·295	0·361	0·463	0·539
27	1·231	25·3	31·0	39·7	46·3	0·311	0·382	0·489	0·570
28	1·241	26·3	32·2	41·2	48·1	0·326	0·400	0·511	0·597
29	1·252	27·3	33·4	42·8	49·9	0·342	0·418	0·536	0·625
30	1·263	28·3	34·7	44·4	51·8	0·357	0·438	0·561	0·654
31	1·274	29·4	36·0	46·1	53·7	0·374	0·459	0·587	0·684
32	1·285	30·5	37·4	47·9	55·8	0·392	0·481	0·616	0·717
33	1·297	31·7	38·8	49·7	57·9	0·411	0·503	0·645	0·751
34	1·308	32·8	40·2	51·5	60·0	0·429	0·526	0·674	0·785
35	1·320	33·9	41·6	53·3	62·1	0·447	0·549	0·704	0·820
36	1·332	35·1	43·0	55·1	64·2	0·468	0·573	0·734	0·856
37	1·345	36·2	44·4	56·9	66·3	0·487	0·597	0·765	0·892
38	1·357	37·2	45·5	58·3	67·9	0·505	0·617	0·791	0·921
39	1·370	38·3	46·9	60·0	70·0	0·525	0·642	0·822	0·959
40	1·383	39·5	48·3	61·9	72·1	0·546	0·668	0·856	0·997
41	1·397	40·7	49·8	63·8	74·3	0·569	0·696	0·891	1·038
42	1·410	41·8	51·2	65·6	76·4	0·589	0·722	0·925	1·077
43	1·424	42·9	52·6	67·4	78·5	0·611	0·749	0·960	1·108
44	1·438	44·1	54·0	69·1	80·6	0·634	0·777	0·994	1·159
45	1·453	45·2	55·4	70·9	82·7	0·657	0·805	1·030	1·202
46	1·468	46·4	56·9	72·9	84·9	0·681	0·835	1·070	1·246
47	1·483	47·6	58·3	74·7	87·0	0·706	0·864	1·108	1·290
48	1·498	48·7	59·6	76·3	89·0	0·730	0·893	1·143	1·333
49	1·514	49·8	61·0	78·1	91·0	0·754	0·923	1·182	1·378
50	1·580	51·0	62·5	80·0	93·3	0·780	0·956	1·224	1·427
51	1·540	52·2	64·0	82·0	95·5	0·807	0·990	1·268	1·477
52	1·563	53·5	65·5	83·9	97·8	0·836	1·024	1·311	1·529
53	1·580	54·9	67·0	85·8	100·0	0·867	1·059	1·355	1·580
54	1·597	56·0	68·6	87·8	102·4	0·894	1·095	1·402	1·636
55	1·615	57·1	70·0	89·6	104·5	0·922	1·131	1·447	1·688
56	1·634	58·4	71·6	91·7	106·9	0·954	1·170	1·499	1·747
57	1·652	59·7	73·2	93·7	109·2	0·986	1·210	1·548	1·804
58	1·671	61·0	74·7	95·7	111·5	1·019	1·248	1·599	1·863
59	1·691	62·4	76·4	97·8	114·0	1·055	1·292	1·654	1·928
60	1·711	63·8	78·1	100·0	116·6	1·092	1·336	1·711	1·995
61	1·732	65·2	79·9	102·3	119·2	1·129	1·384	1·772	2·065
62	1·753	66·7	81·7	104·6	121·9	1·169	1·432	1·838	2·137
63	1·774	68·7	84·1	107·7	125·5	1·219	1·492	1·911	2·226
64	1·796	70·6	86·5	110·8	129·1	1·268	1·554	1·990	2·319
65	1·819	73·2	89·7	114·8	133·8	1·332	1·632	2·088	2·434
66	1·842	81·6	100·0	128·0	149·3	1·503	1·842	2·358	2·750

In this Table the hydrometer-degrees of Baumé were fixed by putting the zero at the immersing-point in pure water, and the degree 66 in pure hydrate of 1·842. This agrees with the formula deduced above.

It would be very desirable, as Hasenclever points out (Hofmann's Report, i. 181), if all sulphuric-acid-makers used the same reduction-tables for their calculations; for in the statements on the yield of acid, and in many other cases, frequently different tables are used; so that the working results of different factories are not always comparable with each other. This very clearly appears from the following comparative Table:—

Degrees (Baumé).	Spec. Grav. (Kolb).	Percentage of SO_4H_2 in the Vitriol according to							
		Vauquelin.	D'Arcet.	Tables of different works.				Bineau.	Kolb.
10	1·075	11·73	...	11·5	11·40	...	10·98	11·0	10·8
20	1·162	24·01	...	23·3	23·46	...	21·97	22·4	22·2
30	1·263	36·52	...	36·9	36·60	...	35·93	34·9	34·7
40	1·383	50·41	...	51·6	51·49	...	49·94	48·4	48·3
50	1·530	66·54	66·45	66·9	66·17	63·8	63·92	62·7	62·5
60	1·711	84·22	82·34	83·3	82·80	79·4	79·90	78·0	78·1
66	1·842	100·00	100·00	100·0	100·00	94·0	97·87	100·0	100·0

The totally incorrect tables of Vauquelin and D'Arcet are used, up to the present time, exclusively in the south of France.

Kohlrausch (Poggend. Ann. Ergänzungsband viii. p. 675) points out that the real hydrate, SO_4H_2, does not present the maximum density of sulphuric acid as all the tables state it, but that, in really pure hydrate, if water be carefully squirted on the top, slowly sinking drops are obtained. He found that the densities of concentrated acid at 18° (water at 4° C.=1) were:—

Per cent. by weight of SO_4H_2.	Specific gravity.	Per cent. by weight of SO_4H_2.	Specific gravity.
90	1·8147	96	1·8372
91	1·8200	97	1·8383
92	1·8249	98	1·8386
93	1·8290	99	1·8376
94	1·8325	100	1·8342
95	1·8352		

According to these observations of Kohlrausch, it appears as if the maximum density of sulphuric acid corresponded exactly, or nearly so, to that acid which distils over unchanged.

The figures given in the tables refer only, of course, to *pure* acid, and cannot be accepted unconditionally as true for the ordinary acid of trade, which always contains impurities. Kolb has examined also into this matter, and has determined the influence of the common impurities upon the density of sulphuric acid, viz. that of lead sulphate, of the oxygen compounds, of nitrogen, and of sulphurous acid. Arsenic, and perhaps iron, usually occur in too small a quantity in sulphuric acid to influence its density; but certainly there may be cases, not mentioned by Kolb, in which vitriol is *strongly* contaminated with salts of iron, aluminium, sodium, &c. The iron, for instance, may come from pyrites-dust, aluminium from the packing of the Glover tower, or from the fire-clay frequently employed for stopping leaks; sodium from solutions of nitrate or sulphate of soda, which sometimes get into the chambers by inadvertence: I have even found zinc in the same in very perceptible quantity after a plumber had emptied his machine direct into the chambers.

For saturated solutions of *sulphurous acid* in sulphuric acid of varying density, Kolb gives the following Table (Bull. Soc. Ind. de Mulhouse, 1872, p. 224)[*]:—

Density of Sulphuric Acid		Quantity of SO_2 dissolved	
Before being saturated with SO_2.	*After* being saturated with SO_2.	Per kilog. Acid.	Per litre Acid.
1·841	1·837	0·009 kilog.	5·8 litres.
1·839	1·831	0·014 „	8·9 „
1·540	1·541	0·021 „	11·2 „
1·407	1·419	0·032 „	15·9 „
1·227	1·244	0·068 „	29·7 „
1·000	1·041	0·135 „	49·0 „

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[*] The Table is corrected by dividing the last column by 10. The necessity of this correction is apparent on calculation, and especially on comparing the last figure (for pure water) with well-known facts. It is remarkable that those copying Kolb's table have not been struck by the contradiction of putting 58 litres of SO_2 per litre sulphuric acid = 9 grms. SO_2 per kilog., &c., and of assuming a solubility of 490 vols. SO_2 in 1 vol. water. Rosenstiehl, in his Report (Bull. Mulh. p. 242), speaks of the 58-fold volume for concentrated acid; and the others follow him. Whether the error rests on a printer's mistake or a miscalculation must be left undecided; but another error in Kolb's large table given above, which *must* be a printer's mistake, and which ought to have been noticed directly, has also been copied unaltered into Dingler's 'Journal' and Wagner's 'Jahresbericht.' The last two figures of the last column but one are given as 2·388 and 2·058; calculation shows that it ought to be 2·088 and 2·358, as here given.

In this Table it strikes the attention that the saturation of *strong* acid with SO_2 somewhat lowers its specific gravity, but rather raises that of *weak* acid; with an acid of 1·540 both tendencies are at an equilibrium and the density is not changed.

In such quantities (up to saturation) sulphurous acid certainly never occurs in commercial vitriol; and it is very rarely that more than traces of it are found therein, since it does not agree with the *nitrogen oxides* which are most frequently found in commercial vitriol. *Nitric acid* is, if at all, only present in extremely small quantities in the vitriol of trade, and therefore does not modify its density to a sensible extent; especially it will not be found in vitriol of more than 144° Tw., except *perhaps* in the nitrous vitriol from the Gay-Lussac towers; but even this, according to my analyses (see below), under normal conditions contains mere traces of NO_3H. *Nitric oxide* can also be neglected; concentrated vitriol does not dissolve it at all; acid of 1·426 sp. gr. only 0·017 per cent. of NO. *Nitrous acid* certainly has a very marked influence on the apparent percentage of a sulphuric acid, according to the hydrometrical test, although only in "nitrous vitriol" such large proportions of nitrous acid occur as to influence the specific gravity of the sulphuric acid. In order to estimate this influence, Kolb conducted into sulphuric acids of different concentrations a mixture of dry air and dry nitric oxide in excess, supposing that it would only yield N_2O_3, not NO_2. His results were as follows*:—

Density of		100 parts of Acid contain				Quantity of SO_4H_2 which *pure* acid would contain if of equal spec. grav. as that saturated with N_2O_3.
Pure Acid.	Acid saturated with N_2O_3.	Before saturation.	After saturation.			
			N_2O_3.	N_2O_5.	SO_4H_2.	
1·841	1·868	99·9	4·25	Traces	94·5	?
1·793	1·814	86·2	4·12	1·28	82·8	89·2
1·749	1·751	81·4	3·90	1·55	76·2	81·4
1·621	1·628	70·7	2·30	1·10	68·6	71·0
1·512	1·519	60·7	0·74	0·31	60·2	61·5
1·426	1·434	52·7	0·25	0·24	53·0	53·6
1·327	1·336	42·2	0·11	0·76	40·8	43·4

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* The occurrence of nitric acid in *concentrated* vitriol, after conducting N_2O_3 into it, is directly contradicted by many experiments of mine, and is possibly to

Nitrogen tetroxide, N_2O_4, need not be taken into account here, as for all analytical purposes it behaves like a mixture of N_2O_3 and N_2O_5.

With respect to *lead sulphate* Kolb found that, at the ordinary temperature, there were dissolved in

100	parts	vitriol of	1·841	spec. grav.	0·039 part.
100	„	„	1·793	„	0·011 „
100	„	„	1·540	„	0·003 „

In more dilute acids the lead can hardly be estimated. Nitric acid, which anyhow occurs in very small quantities, does not strongly influence the solubility of lead sulphate in sulphuric acid, nitrous acid not at all. The influence of lead sulphate on the density of vitriol can accordingly be neglected for the ordinary temperature.

Although, as we see, the impurities of ordinary sulphuric acid, leaving aside "nitrous vitriol," have very little influence on its density, still the latter, at the highest degrees of concentration, is no trustworthy means of estimating the percentage of real SO_4H_2 in the acid, even when the correction for temperature according to the Table on page 26 is applied, because at this concentration a small difference in density corresponds to a very large difference in percentage. Least of all in this case can the ordinary hydrometers be used. Many factories have special hydrometers, in which the last few degrees are spread over a large area and are subdivided further; but anyhow the density ought to be estimated by more accurate methods; for the hydrometers are frequently not reliable, and certainly not so unless the normal temperature for which they have been made be *exactly* observed. But any determination of density for estimating the percentage of the very strongest acids must now be rejected, after Kohlrausch's investigation (p. 28). The acids from 96 per cent. upwards ought therefore always to be estimated alkalimetrically.

The following Table of Anthon's will be of practical value. It shows in column *a* how many parts oil of vitriol of 170° Tw. must be mixed with 100 parts water at 15° or 20°, in order to obtain an acid of the specific gravity *b*.

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be explained by the analytical methods, not quite trustworthy, at that time used (see below); or else the gas, in that case, must have contained NO_2 after all.

a.	*b.*	*a.*	*b.*	*a.*	*b.*
1	1·009	130	1·456	370	1·723
2	1·015	140	1·473	380	1·727
5	1·035	150	1·490	390	1·730
10	1·060	160	1·510	400	1·733
15	1·090	170	1·530	410	1·737
20	1·113	180	1·543	420	1·740
25	1·140	190	1·556	430	1·743
30	1·165	200	1·568	440	1·746
35	1·187	210	1·580	450	1·750
40	1·210	220	1·593	460	1·754
45	1·229	230	1·606	470	1·757
50	1·248	240	1·620	480	1·760
55	1·265	250	1·630	490	1·763
60	1·280	260	1·640	500	1·766
65	1·297	270	1·648	510	1·768
70	1·312	280	1·654	520	1·770
75	1·326	290	1·667	530	1·772
80	1·340	300	1·678	540	1·774
85	1·357	310	1·689	550	1·776
90	1·372	320	1·700	560	1·777
95	1·386	330	1·705	580	1·778
100	1·398	340	1·710	590	1·780
110	1·420	350	1·714	600	1·782
120	1·438	360	1·719		

On mixing oil of vitriol with water a considerable rise of temperature takes place, water being chemically fixed by the formation of certain hydrates, as described above. Besides, on mixing concentrated acid with water, as already mentioned, a not inconsiderable contraction takes place, which must equally lead to an evolution of heat. But on mixing strong vitriol with snow a strong cold is produced by the heat becoming latent on the liquefaction of snow, which considerably exceeds that becoming free in consequence of the chemical combination. This cold, however, is only produced when the proportion between acid and ice does not exceed certain limits: for 1 part of vitriol there must be 1¼ part of snow present; with less snow there is a rise of temperature.

Although there is nothing to show that hydrates of sulphuric acid exist with more than 2 H_2O to 1 SO_4H_2, even at stronger dilution much heat is liberated, as proved by the experiments of Graham, Hess, Abria, Favre, Silvermann, Andrews, Thomsen, &c.

The evolution of heat has been computed by Favre and Quaillard (Compt. Rend. l. 1150):—for the mixture of 1 gr. sulphuric monohydrate, SO_4H_2, with

The first ⅛	molecule of water . .	9·66	metrical units of heat.
,, second ⅛	,, ,,	9·04	,, ,,
,, second ¼	,, ,,	17·45	,, ,,
,, second ½	,, ,,	28·90	,, ,,
1	,, ,,	66·44	,, ,,
2	,, ,,	99·54	,, ,,
3	,, ,,	118·33	,, ,,
4	,, ,,	130·36	,, ,,
5	,, ,,	139·39	,, ,,
6	,, ,,	146·39	,, ,,
7	,, ,,	152·43	,, ,,
8	,, ,,	157·18	,, ,,
12	,, ,,	168·03	,, ,,
16	,, ,,	172·96	,, ,,
20	,, ,,	175·23	,, ,,
24	,, ,,	176·67	,, ,,
28	,, ,,	177·56	,, ,,
32	,, ,,	178·22	,, ,,
36	,, ,,	178·66	,, ,,
40	,, ,,	178·99	,, ,,

Even on adding the sixtieth molecule of water, sulphuric acid still gives out a sensible quantity of heat.

Thomsen (Deutsch. chem. Ges. Ber. iii. 496) gives the following Table :—

x.	$H_2SO_4+xH_2O$.
1	6272 heat-units.
2	9364 ,, ,,
3	11108 ,, ,,
5	13082 ,, ,,
9	14940 ,, ,,
19	16248 ,, ,,
49	16676 ,, ,,
99	16850 ,, ,,
199	17056 ,, ,,
499	17304 ,, ,,
799	17632 ,, ,,
1599	17848 ,, ,,

On account of this considerable evolution of heat, concentrated vitriol and water must always be mixed with care: the water ought never to be poured into the acid, but the acid run in a thin jet into the water with constant stirring. On a sudden mixture, so much heat is liberated at once that the acid may be raised to the boiling-point and splash about; and glass vessels are easily cracked thereby.

The affinity of vitriol for water is also proved by its great hygroscopicity. Concentrated vitriol is one of the best means for drying gases; and it is not only used in this way for innumerable scientific, but also for some technical purposes—for instance, in the manufacture of chlorine by Deacon's process, where the gaseous mixture, having been deprived of its hydrochloric acid by water, is passed through a coke-tower fed with sulphuric acid, in order to be deprived of its moisture. In the same way, chlorine gas is dried for the process of utilizing tinned scrap-iron by treatment with chlorine, which in the dry state does not act upon iron, but gives with tin anhydrous tin tetrachloride.

Concentrated sulphuric acid acts also upon liquid and solid bodies by depriving them of water or even splitting off the elements of the same if the substance only contains the latter but no readily formed water. Upon this action, too, a host of scientific and technical applications of sulphuric acid are founded. In this case frequently the so-called *sulphonic acids* are formed, generally compounds easily lending themselves to further reactions. Instances of this are:—the formation of ether by the splitting-up of sulphuric acid, with the intermediate formation of sulphovinic acid; that of ethylene on the further splitting-off of water; the preparation of nitrobenzene, picric acid, nitronaphthaline, all through the sulphonic acids; the manufacture of resorcine and alizarine by the alkaline fusion of the sulphonic acids of benzene and anthraquinone, and many other cases.

The charring of many organic substances, such as wood, sugar, &c., by contact with strong vitriol, is derived from the same source. Necessarily this acid, in its concentrated form, must have an extremely prejudicial action on the animal body. The remedy usually applied, viz. burnt magnesia, cannot do much good when the epithelium of the œsophagus and the stomach are once destroyed.

The affinity of concentrated vitriol for water is also shown by the fact that it easily runs over, when kept in open vessels, by attracting moisture from the air—a fact to keep in view in the case of balances &c.

The *melting-points* of sulphuric acids of different degrees of concentration are given by Payen as follows (but not all of his statements agree with the results of more recent researches as quoted above):—

		°C.
Anhydride, α modification	melts at	+ 18
„ β „	„	+100
Subhydrate (pyrosulphuric acid)	„	+ 35
Monohydrate, SO_4H_2	„	+ 10·5
The same with a very small addition of anhydride	„	− 20
The same, with a very little water (ordinary oil of vitriol)	„	− 20 to − 30
Dihydrate	„	+ 8·5
Sulphuric acid containing, to 1 molecule of acid, 3 molecules of water or more, remains liquid at	„	− 20
The same, *in vacuo*	„	− 40

On boiling dilute sulphuric acid, at first nothing but aqueous vapour escapes; according to Graham, only then is acid vapour mixed with the steam, when no more than 2 molecules of water are present to 1 of SO_3—that is, with a percentage of 84·48 SO_4H_2 or a specific gravity of 1·78. After several discussions about the loss of sulphuric acid in concentrating it, by the author, Bode, Walter, &c., it may be assumed that in manufacturing practice no sensible loss of acid takes place by real *volatilization* up to a strength of 144° or even of 152° Tw.; but on strong boiling there is always a little acid carried away mechanically in the shape of small drops, especially in pans fired from the top and also in the Glover tower. When the evaporation up to that point takes place quietly at a moderate heat there is probably no loss of acid at all.

The *boiling-points* of sulphuric acid of different strengths have been stated by Dalton as follows:—

Specific gravity.	Boiling at	Specific gravity.	Boiling at	Specific gravity.	Boiling at
	° C.		° C.		° C.
1·850	328	1·810	245	1·699	190
1·849	318	1·801	240	1·684	186
1·848	310	1·791	230	1·670	182
1·847	301	1·780	224	1·650	177
1·845	293	1·766	217	1·520	143
1·842	284	1·757	212	1·408	127
1·838	277	1·744	204	1·300	116
1·833	268	1·730	198	1·200	107
1·827	260	1·715	194	1·100	103
1·829	253				

It stands to reason that this Table, made in the beginning of this century, requires revising; so much is certain, that the specific gravity of the monohydrate is assumed too high, and its boiling-point agrees neither with the statement of Marignac (338°) nor with that of Pfaundler (317°). The author has therefore again examined this matter (Ber. d. deutsch. chem. Ges. xi. 370), and has found the following result:—

TABLE I.

Specific gravity.	Temperature. ° C	Spec. grav. reduced to 15° C.	Percentage of SO_4H_2.	Boiling-point. ° C.	Barometer reduced to 0°. Millims.
1·8380	17	1·8400	95·3	297	718·8
1·8325	16·5	1·8334	92·8	280	723·9
1·8240	15·5	1·8245	90·4	264	720·6
1·8130	16	1·8140	88·7	257	726·0
1·7985	15·5	1·7990	86·6	241·5	720·1
1·7800	15	1·7800	84·3	228	720·5
1·7545	16	1·7554	81·8	218	726·0
1·7400	15	1·7400	80·6	209	720·6
1·7185	17	1·7203	78·9	203·5	725·9
1·7010	18	1·7037	77·5	197	725·2
1·6750	19	1·6786	75·3	185·5	725·2
1·6590	16	1·6599	73·9	180	725·2
1·6310	17	1·6328	71·5	173	725·2
1·6055	17	1·6072	69·5	169	730·1
1·5825	15	1·5825	67·2	160	728·8
1·5600	17	1·5617	65·4	158·5	730·1
1·5420	17	1·5437	64·3	151·5	730·1
1·4935	18	1·4960	59·4	143	730·1
1·4620	17	1·4635	56·4	133	730·1
1·4000	17	1·4015	50·3	124	730·1
1·3540	17	1·3554	45·3	118·5	730·1
1·3180	17	1·3194	41·5	115	730·1
1·2620	17	1·2633	34·7	110	732·9
1·2030	17	1·2042	27·6	107	732·9
1·1120	17	1·1128	15·8	103·5	732·9
1·0575	17	1·0580	8·5	101·5	735·0

TABLE II.

(Calculated by graphical interpolation.)

Per cent. SO_4H_2.	Boiling-point.	Per cent. SO_4H_2.	Boiling-point.	Per cent. SO_4H_2.	Boiling-point.	Per cent. SO_4H_2.	Boiling-point.
5	101°	45	118°·5	70	170°	86	238°·5
10	102	50	124	72	174·5	88	251·5
15	103·5	53	128·5	74	180·5	90	262·5
20	105	56	133	76	189	91	268
25	106·5	60	141·5	78	199	92	274·5
30	108	62·5	147	80	207	93	281·5
35	110	65	153·5	82	218·5	94	288·5
40	114	67·5	161	84	227	95	295

Formation of Sulphuric Acid.—It is not probable, though it has been asserted, that sulphuric acid is formed in damp flowers of sulphur, even at the ordinary temperature; but this is said to be the case on heating sulphur with water to 200° C., or by the electric current. Sulphur is easily oxidized to sulphuric acid by chlorine, hypochlorous acid, nitric acid, aqua regia, &c. It is produced, along with sulphurous acid and sulphur, from tri-, tetra-, and pentathionic acids—from the former by merely heating, from all three by the action of chlorine or bromine, or even on the prolonged action of stronger acids, which set the thionic acids free; also hyposulphites yield sulphuric acid under the action of chlorine. All these decompositions have to be kept in view in alkali-making.

Mostly sulphuric acid is formed from sulphurous acid. The aqueous solution of the latter is gradually transformed into sulphuric acid by the action of the air alone, is transformed at once by chlorine, bromine, iodine, hypochlorous acid, nitric acid, and several metallic salts, such as manganic sulphate, mercurous nitrate, &c. Sulphur dioxide and oxygen conducted through a red-hot tube containing platinum, platinized asbestos, ferric oxide, &c., in the presence of water yield sulphuric acid, in its absence sulphuric anhydride. Far more important than all these cases is the formation of sulphuric acid from sulphurous acid by atmospheric oxygen, nitrous acid acting as the carrier of the latter. This is the foundation of the manufacture of sulphuric acid, and will be explained in detail later on.

Decompositions of Sulphuric Acid.—Some of these have been mentioned already—for instance, that into anhydride and water by evaporation. The mixed vapour, on account of the unequal velocity of diffusion of the two vapours, can be separated to a great extent into its two constituents, so that at 520° C., in an hour, a residue of 60 per cent. monohydrate and 40 per cent. anhydride, at 445° C. 75 per cent. monohydrate and 25 per cent. anhydride was obtained (Wanklyn and Robinson, Proc. Roy. Soc. xii. p. 507). Perhaps a process for preparing fuming acid can be founded upon this fact. Even far below the boiling-point the dissociation begins in the liquid acid. It has been pointed out that already at 30° to 40° C. the hydrate begins to give off vapours of anhydride (Marignac), which fact has been confirmed by the exact researches of Dittmar (Chem. Soc. Journ. [2] vii. p. 446) and Pfaundler and Pölt (Zeitschr. f. Chemie, xiii. p. 66).

A furthergoing decomposition into sulphur dioxide, oxygen, and water takes place on conducting the vapour of sulphuric acid through porcelain or platinum tubes, filled with bits of porcelain and heated to a bright red heat. This mode of decomposition has been recommended by Deville and Debray as a "cheap" plan for making oxygen; but it does not seem to have answered, owing to the insufficient sale for sulphurous acid or its salts; perhaps it will play a great part in future for the manufacture of anhydride by Winkler's process.

On heating with charcoal to 100° or up to 150° C., sulphuric acid yields carbon dioxide and sulphur dioxide; on boiling with phosphorus, sulphur; on boiling with sulphur, sulphur dioxide; by the action of the electric current, hydrogen, oxygen, sulphur, &c. (in dilute sulphuric acid the electric current merely causes the decomposition of water).

Sulphuric acid in the cold, and at temperatures below its boiling-point, is the strongest of all acids, and expels all other acids from their salts when the solubilities &c. allow this; but, inversely, sodium sulphate is also decomposed by hydrochloric acid. Boussingault (Ann. Chim. Phys. [5] ii. p. 120) has shown that dry hydrochloric-acid gas at a red heat decomposes the sulphates of sodium, potassium, barium, strontium, and calcium (see further on). More refractory acids expel sulphuric acid at higher temperatures—for instance, boric acid, silica, and phosphoric acid.

With the bases sulphuric acid forms two principal series of salts, viz. acid ones, of the formula $SO_2 \begin{smallmatrix} \diagup OH \\ \diagdown OM \end{smallmatrix}$, and neutral ones, of the formula $SO_2\langle\begin{smallmatrix}OM\\OM\end{smallmatrix}$. Very frequently it also occurs in basic salts, rarely in hyperacid salts.

The technical applications of sulphuric acid to a great extent rest on its great affinity to all bases. Of its salts the acid and neutral ones are soluble in water, excepting the neutral salts of barium, strontium, lead, silver, and mercury (in the state of protoxide), which are little or not at all soluble in water and dilute acids. Calcium sulphate is sparingly soluble in water. Most sulphates are insoluble in alcohol. The *basic* sulphates are mostly insoluble in water, but soluble in acids. The sulphates incline very much towards the formation of double salts, of which those are called *alums* which contain a combination of univalent and trivalent (corresponding to a double atom of quadrivalent) metals.

The neutral salts of the alkali-metals, of calcium, magnesium, silver, manganese, and ferrosum, the latter only if entirely free from acid and peroxide (a condition very rarely realized), do not redden blue litmus paper, whilst all other soluble sulphates do this.

On *heating* to a red heat, only the neutral sulphates of the alkalies, of the alkaline earths, and of lead remain unchanged. At a still higher temperature (that of melting iron) the two latter classes are also decomposed, but the alkaline sulphates are volatilized without a change. Even zinc and manganous sulphate are so difficult to decompose that in practical work they are considered as fireproof in most cases. This explains the difficulty of completely converting blende into oxide of zinc.

On roasting, the decomposable sulphates yield metallic oxides, sulphur dioxide, and oxygen. They are much more easily split up on heating by certain additions, such as coal, iron, &c.

On the metals sulphuric acid acts in a very different way. The water-decomposing metals in the cold yield nothing but hydrogen with it; in the hot even zinc and iron already yield sulphurous acid; and zinc, if certain conditions are observed, can even yield sulphuretted hydrogen (Fordos and Gélis).

Most of the heavy metals do not act upon sulphuric acid in the cold and in a dilute state; they yield sulphur dioxide only on being heated with *concentrated* acid, such as arsenic, antimony, bismuth, tin, lead, copper, mercury, silver (sulphates being formed at the same time); gold, platinum, iridium, and rhodium do not act on sulphuric acid at any temperature.

Apart from the inaction of pure sulphuric acid on platinum, the behaviour of vitriol towards lead and cast iron is especially of technical interest.

Cast iron is very little acted upon by concentrated vitriol, either hot or cold. For many years now, cast-iron vessels have been employed for boiling sulphuric acid with silver, for making nitrobenzene by a mixture of sulphuric and nitric acid, for pumping vitriol by compressed air, &c. In the cold, and at a gentle heat, even moderately dilute vitriol acts very little on cast iron; it can be used for pumping chamber-acid onto the Glover tower, and even for the preliminary heating of the vitriol in the manufacture of saltcake.

Balmain and Menzies have indeed proposed to send out sulphuric acid in iron vessels, in lieu of the usual glass carboys; it should not, however, be below 130° Tw., should not contain any impurities acting upon iron, and it must not be left in contact with air in the vessels. In this case even wrought-iron vessels can be employed. (Compare the end of Chap. XIII.)

The action of sulphuric acid on *lead* has been examined several times. This matter is of very great importance for the manufacture of sulphuric acid. The best-known research is that of Calvert and Johnson (Compt. Rend. lvi. p. 140). Most metals are all the less acted upon by acids the purer they are; but the contrary seems to be the case with lead. Calvert and Johnson allowed sulphuric acid of different concentration to act at the ordinary and at higher temperature on three different kinds of lead, viz.:—A, ordinary lead (with 98·8175 Pb, 0·3955 Sn, 0·3604 Fe, and 0·4026 Cu); B, virgin lead (with 99·2060 Pb, 0·0120 Sn, 0·3246 Fe, 0·4374 Cu); and, C, chemically pure lead. Plates of 1 metre square each were covered with 16 litres of sulphuric acid each; and after ten days the quantity of lead sulphate formed was estimated. In the first four experiments pure acid was used, in the last two such acid as it is obtained in acid-works by concentration in lead pans. In these two experiments the temperature was 48° to 50°.

	Spec. grav. of the acid employed.	Ordinary lead. grms.	Virgin lead. grms.	Pure lead. grms.
I.	1·842	67·70	134·20	201·70
II.	1·705	8·35	16·50	19·70
III.	1·600	5·55	10·34	16·20
IV.	1·526	2·17	4·34	6·84
V.	1·746	49·67	50·84	55·00
VI.	1·746	51·91	54·75	57·41

The result is that lead is all the more acted upon the purer it is, and that an energetic action only takes place above the specific gravity of 140° Tw.

Mallard (Bull. Soc. Chim. 1874, ii. p. 114) experimented with lead containing 99·62 Pb, 0·14 Sb, 0·03 Fe, 0·21 not estimated, and with ordinary commercial acid. At a strength of 148° Tw. and the corresponding boiling-point 205° C. it acts upon the lead, yielding SO_2 and $Pb\,SO_4$. Above 148° Tw. and up to 166° Tw. (boiling-point 320° ?) at the same time sulphur is formed ($SO_2 + 2Pb = S + Pb\,O$).

Hasenclever (Ber. d. deutsch. chem. Ges.) employed very pure soft lead from Mechernich, with 99·9941 Pb, 0·0006 Ag, 0·0008 Cu, 0·0040 Sb, 0·0005 Fe, which he heated in a flask with sulphuric acid of 120° Tw. Already at 40° C. small gas-bubbles rose from the lead; at 80° a perceptible evolution of H and H_2S took place; and this increased at higher temperatures. The same lead, melted up with some antimony and again exposed to pure vitriol of 120° Tw. caused at 85° only a scarcely visible, at 100° a just perceptible, and not below 140° a strong evolution of gas. This agrees with Calvert and Johnson's experiments.

Lastly, Bauer (Ber. d. deutsch. chem. Ges. 1875, p. 210) has examined this matter. He employed several alloys of certain composition and vitriol of 170° Tw. When the acid already contained dissolved lead sulphate, a higher temperature was required for the action. The results were as follows:—

1. Pure lead. 0·2 grm. heated with 50 cub. centims. acid of 170° Tw. First sensible evolution of gas at 175° C., stronger at 190°; at 230–240° C. suddenly all the lead is changed into sulphate, which dissolves in the acid, SO_2, H, and S being observed.

2. Lead and bismuth. (*a*) 90 Pb, 10 Bi: action beginning at 150°, goes on slowly and quietly up to 190°, when all the metal is

decomposed. (*b*) 96 Pb, 4 Bi: decomposition quicker than in *a*, terminated at 130–140°. (*c*) 99·27 Pb, 0·71 Bi: decomposition rapid and sudden at 160°.

3. Lead and antimony. (*a*) 10 per cent. Sb: slow and even decomposition, beginning at 190°, ending between 230° and 240°. (*b*) 5 per cent. Sb: slow decomposition, beginning at 180–190°, ended at 220–225°. (*c*) 1 per cent. Sb: slow decomposition, just perceptible at 250°, ended at 280° C.

4. Lead and arsenic (10 per cent. As). Process similar to the alloy with 10 per cent. Sb; ended at 240°.

5. Lead with 1 per cent. copper behaves similarly to lead with 1 per cent. Sb; stronger action beginning at 250°, all the metal dissolved at 280°.

6. Lead and platinum. (*a*) 10 per cent. Pt: slow, incomplete decomposition, ended at 280°. (*b*) 2 per cent. Pt: sudden decomposition, complete between 260° and 280°.

7. Lead with 10 per cent. tin. Process similar to pure lead; sudden decomposition at 200° C.

From this it would seem as if small quantities of antimony and copper made the lead more resisting, and as if bismuth acted the other way.

In the north of England those rolling mills which roll the sheet-lead for the many large vitriol-works supply a special kind of "chemical lead" which is made from the melted-up old chamber-lead, pipes, &c.; in this case many impurities, especially antimony, from "regulus"-valves, &c., get into the lead, which seems to improve its quality for acid-chambers.

CHAPTER II.

ANALYSIS OF SULPHURIC ACID.

QUALITATIVELY sulphuric acid is always recognized best by the white precipitate of barium sulphate which it gives with barium chloride, both in the free state and in the solutions of its salts, even when very much diluted. This precipitate mostly settles down as a heavy powder, but in extremely dilute liquids sometimes appears only after some little time as a white cloud. Barium sulphate is as good as insoluble in water, solutions of salts, and free dilute acids; in concentrated acids it is a little soluble, especially on heating, also in concentrated sulphuric acid itself. On the other hand, in a very concentrated liquid free from sulphuric acid, but containing much hydrochloric or, especially, nitric acid, the addition of barium chloride may cause a precipitate of barium chloride itself or of barium nitrate, which, however, is distinguished from barium sulphate by its crystalline appearance, and even more by vanishing on dilution of the liquid; barium seleniate is distinguished from barium sulphate by its solubility on boiling with concentrated muriatic acid, and by its behaviour with the blow-pipe. This reaction proves the presence of sulphuric acid either in its free state or in its salts; but of course it can no longer do this when the sulphuric acid has combined with organic substances to form "sulphonic acids," just because these contain neither sulphuric acid as such nor sulphates. In order to find sulphuric acid in the *free* state in the presence of sulphates of acid reaction, either the alcoholic solution of the substances can be tried with barium chloride (free acid being soluble, but all sulphates insoluble in spirit of wine), or the charring properties of concentrated oil of vitriol are made use of by evaporating the solution mixed with a little cane-sugar in a small porcelain capsule on the water-bath, and observing whether a blackening of the sugar takes place. This reaction, however, also takes place with the sulphates of very weak bases, such as alumina or ferric oxide; also sulphuric acid cannot be distinguished with certainty in this way from hydrochloric or nitric acid; but in phosphoric, acetic, tartaric acid, &c. a very small proportion of sulphuric acid can be proved by this reaction. The best reaction for free sulphuric acid, as well as for any strong free acid, is that with an azo-compound, such as amidoazobenzene, tropæoline, Poirier's orangé, &c.; these do not change their colour by metallic salts, but by the smallest quantity of *strong* free acid. Carbonic and acetic acids, or sulphuretted hydrogen, do not act upon them (see p. 48).

In insoluble sulphates the acid is recognized by fusing them with alkaline carbonates, or by boiling with concentrated solutions of the same and filtering the solution of the alkaline sulphate formed thereby from the insoluble carbonates, or with the blowpipe, on charcoal, by the formation of sodium sulphate, according to well-known methods.

The quantitative estimation of free sulphuric acid for technical purposes is almost exclusively effected by volumetric methods or by the hydrometer. In both cases, of course, impurities will have a disturbing action; but for technical purposes they may nearly always be neglected, as Kolb has shown (compare p. 29). The hydrometric estimation of sulphuric acid has been already described in detail; and we must here only point out again that the temperature must not be neglected in this case. The figures of the hydrometer may be reduced to the normal temperature by Bineau's formula (p. 26); but it is better to bring the acid to a temperature approaching the normal temperature, by putting the vessel either into warm or into cold water, as the case may require.

The volumetrical estimation of free acid generally takes place by means of a standard solution of potash, soda, or ammonia, using tincture of litmus as an indicator. According to the accuracy required, either a normal solution is used (that is, one containing per litre an equivalent expressed in grams), or a semi- or decinormal solution, &c. Some prefer ammonia, because it attracts but little carbonic acid, which makes the reaction with litmus less sharp; but its volatility is a drawback to ammonia solution, its smell proving a constant although minute loss. In dilute solutions (a stronger solution than seminormal ammonia ought never to be used) and in closed bottles this amounts to very little; but still it is not advisable to choose this liquid for very accurate work. As between caustic soda and caustic potash, Mohr prefers the latter, because the former causes cracks in the burettes. This is certainly true; but the author has used a soda-burette cracked all over for a dozen years without any drawback. Of course some contrivance must be used for depriving the air entering the burette of its carbonic acid. A very suitable form of apparatus for this purpose is shown in fig. 1 (p. 46).

This apparatus can even be used with baryta-water as acidimetrical liquid, and works perfectly satisfactorily.

As indicator, nearly always, tincture of litmus is used, prepared by digesting litmus with six times its weight of water at the ordinary or a slightly higher temperature, pouring off the clear liquid, and filtering; sometimes a little spirit of wine is added to it. In order to obtain a sharp reaction, the solution, which is generally too alkaline, ought to be divided in halves: one half is stirred up with a glass rod dipped in dilute nitric acid, till its colour has changed from blue through purple into pure red; the other half is then added to it; and the purple mixture ought to be so sensitive that a quantity of pure water coloured strongly by it will be stained distinctly red by the least trace of an acid, and blue by a trace of alkali. The litmus-solution decomposes on keeping in closed vessels; it must therefore be kept in a loosely covered bottle. A very convenient form for it is that represented in fig. 2, which allows of running out as many drops as desired without inclining the bottle or losing any litmus.

An alcoholic solution of *coralline* has the advantage of greater sensitiveness and durability than litmus. The transition from the beautiful purple-red of the alkaline liquid to the almost colourless acid liquid is very striking, and probably visible to some persons colour-blind for litmus.

Litmus is not well adapted for working in artificial light: the red appears almost as clear as water, the blue like a dark violet; but the transition from bright red into purple &c. cannot be seen with certainty. This can be remedied by monochromatic light if the artificial light be coloured yellow by common salt: the red appears clear as water, the blue like deep black; and the transition is even sharper than in daylight.

Quite recently W. von Miller (Ber. d. deutsch. chem. Ges. xi. p. 460) has proposed, as an indicator for alkalimetry and acidimetry,

Fig. 1.

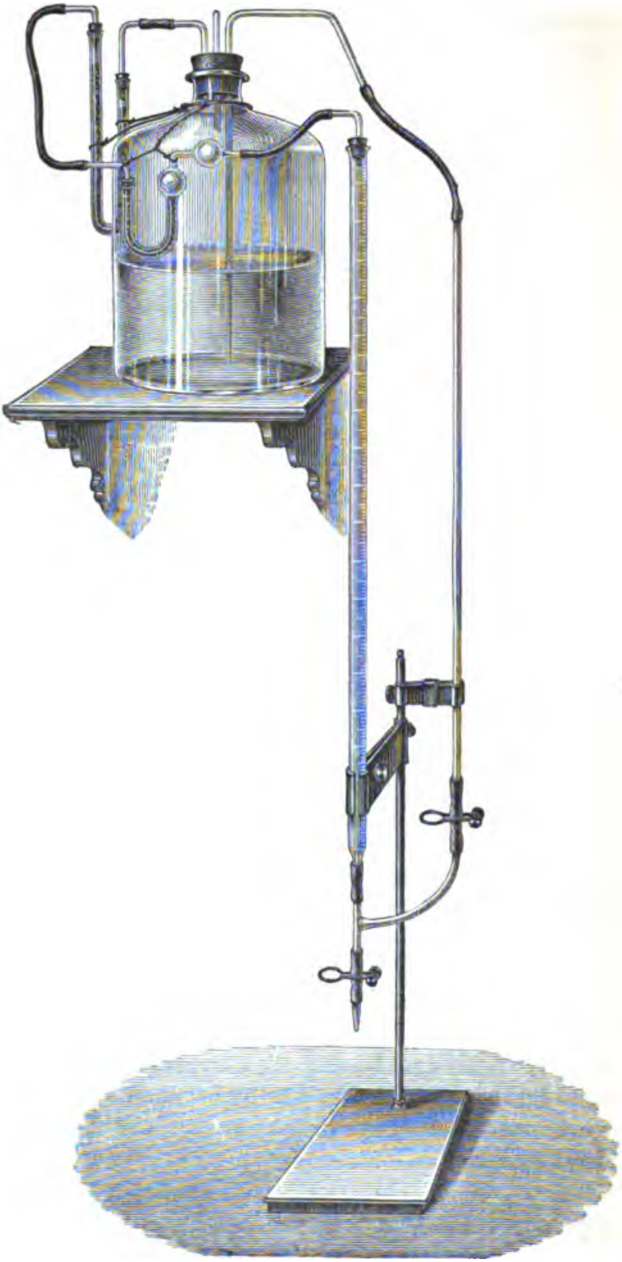
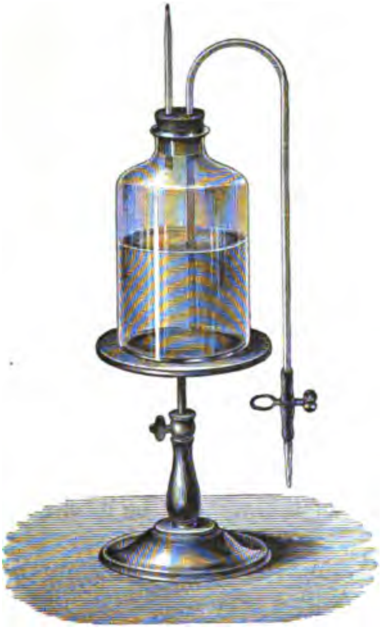


Fig. 2.



tropæoline, a coal-tar dye discovered by O. N. Witt, and brought out by Messrs. Williams, Thomas, and Dower, of London. The brand marked OO is best adapted for this purpose. Of this a watery solution of 0·1 per cent. is made; and 2 cub. centims. of this are taken for each 50 cub. centims. of the liquid to be titrated. This solution yields with alkaline solutions a bright-yellow liquid, which, on adding acid to it, suddenly changes into reddish yellow. The next drop of acid (which is not to be calculated) transforms the colour into a decided red. The change of colour is very sharp, though not more so than in the case of litmus; but tropæoline has a very great advantage above litmus in this, that the yellow colour of its watery solution is not changed by either bicarbonates or free carbonic acid. Alkaline carbonates can therefore be titrated with it *without heating*; and instead of a normal solution of a caustic alkali, one of *sodium carbonate* can just as easily be used for titrating acids. The solution of tropæoline has the further advantage over litmus of not being reddened by any neutral metallic salts, but only by free acids; thus traces of the latter in salts of aluminium, iron, &c. can be detected and estimated. The author can recommend tropæoline from his own experience. He has, moreover, found that many other azo-compounds do the same service; and of these especially the orangé III. of Poirier and the amidoazobenzene can be recommended. The latter must be used in alcoholic solution. With the former the change of colour is still more marked than with tropæoline; and the latter is much less sensitive than most other azo-dyes to sulphuretted hydrogen, which certainly principally comes into play in titrating soda, black ash, &c.

The normal alkaline solution itself is best standardized by means of a normal acid, be it sulphuric, oxalic, or hydrochloric acid; and this on its part is best standardized by pure ignited sodium carbonate, which is easily obtained or prepared—for instance, by washing and igniting sodium bicarbonate. If sodium carbonate, bought as chemically pure, dissolves in water without any residue, and shows by the ordinary reagents no chloride or sulphate, or only unweighable traces of these, it can be used at once for standardizing normal acids after moderately igniting. If tropæoline be used as indicator, this roundabout way need not be taken, but pure soda itself can be used as acidimetrical liquid, either in a normal solution containing 53 grams per litre, or in more dilute solutions.

As normal acid most works use sulphuric acid—against which nothing can be said, except that it is not adapted for titrating bodies yielding insoluble sulphates. But a similar objection must be made to oxalic acid, so warmly recommended by Mohr. This cannot be recommended as a general alkalimetrical liquid in factories, because it is somewhat expensive if "pure," because its durability in dilute solutions is very limited, and because even the so-called "pure" oxalic acid is rarely perfectly pure, let alone the uncertainty about the exact percentage of water of crystallization. In spite of the troublesome plan for purifying it recommended by Mohr, oxalic acid cannot be relied upon as the *foundation* of alkalimetry or of acidimetry; and if this reason for using it lapses, the only remaining one is that, apart from alkalimetry, oxalic acid renders important service in titrations with permanganate of potash, in the analysis of manganese, and especially in the testing of the Weldon muds &c. But it is certainly preferable to keep a separate burette for this purpose, and to use sulphuric or else hydrochloric acid for the daily testings of soda-ash &c. Nitric acid might also be used; and it has this advantage, that after neutralization by it the chlorides can be estimated in the liquid by silver nitrate, as will be explained when we describe the testing of soda-ash; but the metallic pinchcocks do not stand its use, and it requires special forms of burettes or glass cocks.

Since in a laboratory the normal acids frequently have to be restandardized, it is best to make a solution of exactly 53 grams of ignited sodium carbonate in a litre of water (apart from the use of such a liquid with tropæoline &c. as indicator). This solution is kept in a stoppered bottle; and, for each testing, 10, 20, or 50 cub. centims. are taken out by means of a pipette, after shaking up the contents of the bottle in order to mix again any water evaporated and condensed in the upper part of the bottle. For the most accurate estimations it is always preferable to weigh each portion of sodium carbonate, directly after igniting and cooling, into the beaker, since it is never possible to measure as accurately as to weigh, because, among other reasons, the volumetrical apparatus very rarely agree quite accurately with one another. In spite of the trouble, it should not be neglected to compare, in the first instance, the pipettes with all the measuring-flasks, in order to see whether the former fill the latter precisely; secondly, to calibrate the burettes accurately, in which case it will often be found that the upper parts differ by several per cent. from the middle and lower ones, and cause a corresponding error. Of course the burettes must again be compared with the other measuring-apparatus. Lastly, the *measures* of the burettes, pipettes, &c. must be compared with the *weights* of water corresponding to them. In these tests the apparatus, even of first-class makers, often show large deviations, which may cause gross errors in analyses, and sometimes unpleasant disagreements with other analysts. But as to the *weights* from respectable makers, these are nearly always so near the truth that their deviations from it do not count in comparison with the unavoidable experimental errors.

The standard acid is made to represent *equivalents*, not molecules; that is, if sulphuric or oxalic acid, it will contain one half of the molecular weight in grams, viz. 49 or 63 grams, because these acids are bivalent; but if the univalent muriatic or nitric acid, it will contain the total molecular weight, viz. 36·46 grams HCl, or 63 grams NO_3H. First of all, the acid is diluted a little less than necessary, and it is found out how many cub. centims. of it are required for a certain quantity of sodium carbonate. From this the quantity of water is computed which is required for obtaining an exactly normal acid; and after mixing this with the acid the accuracy of the standard is ascertained by repeated titrating with sodium carbonate. Not less than 2 to 3 grams of the latter, or 50 cub. centims. of a normal solution of it (53 grams per litre), should be taken for each test. To the alkaline solution drops of tincture of litmus are added till it becomes very markedly blue, then acid till strong effervescence sets in; and the liquid is now made to boil; then to the hot liquid gradually more and more acid is added, till the blue colour has passed through the purple and reddish purple of the CO_2 reaction to the bright red of the SO_4H_2 reaction. The liquid cooled by the addition of acid must be constantly heated again. Often, after several minutes' boiling, the apparently red liquid again turns purple and then blue. When working with boiling liquids there is never any doubt, to a single drop, upon the point where the pure red sets in. All this trouble is saved by employing tropæoline &c. as indicator and working in the cold.

When a perfectly accurate normal acid has been obtained, the normal alkali, whether ammonia, soda, or potash, is most easily made from it; and this is now used for the acidimetric test of sulphuric acid. Concentrated vitriol must, of course, first be diluted in the usual manner.

The estimation of sulphuric acid in sulphates will be explained further on when describing the assaying of pyrites.

The impurities of sulphuric acid are recognizable *qualitatively* in the following manner:—A *residue* on evaporating sulphuric acid in a platinum crucible may contain sulphates of sodium (more rarely of potassium), of calcium, aluminium, iron, lead; copper, zinc, or other metals occur rarely in sensible quantity. The individual substances are sought for by the ordinary analytical methods. *Iron* is already betrayed by the colour of the residue after ignition, and can also be detected in the acid itself, without evaporating it, by the ordinary reagents, such as potassium, ferrocyanide, potassium sulphocyanide, &c. *Lead* is often shown as a white precipitate of sulphate on diluting concentrated vitriol with water—further, by adding one or two drops of hydrochloric acid, by which white clouds are formed, which vanish on addition of more hydrochloric acid or on heating; with more certainty it is shown by diluting (even weaker acid) with three or four times its volume of strong alcohol. The precipitate must, of course, be examined further—for instance, with the blowpipe, by reduction on charcoal to metallic lead, by moistening with ammonium (which blackens it), &c. *Selenium* can be found in dilute sulphuric acid by reduction with SO_2, or by precipitation with H_2S. The yellow selenium sulphide is distinguished from arsenic sulphide by its insolubility in ammonia and by its behaviour with the blowpipe. Selenium will also be mentioned when speaking of the nitrogen oxides. *Thallium* is only recognized with certainty by the spectroscope. *Arsenic* is recognized by sulphuretted hydrogen in a dilute solution, more safely by Reinsch's test—diluting with equal volumes of water and pure hydrochloric acid, and immersing bright copper foil, which, after gentle heating, is covered with a fast-adhering slate-grey precipitate, which, according to Lippert, is a compound of copper and arsenic, Cu_5As_2 (if the arsenic is present as arsenic acid, the reaction only sets in after longer heating); further, by Marsh's apparatus, in which, by means of pure zinc and water, the arsenic is given off as arseniuretted hydrogen, and is proved by reduction in a red-hot tube, or by lighting the gas and holding a piece of porcelain in the flames, on which any arsenic appears as spots.

Since it is difficult to procure zinc absolutely free from arsenic, it is well to substitute aluminium foil for it. There may be arsenic acid as well as arsenious acid present; this can be proved by neutralizing with ammonia and adding magnesia mixture: any precipitate must contain the arsenic acid, the filtrate the arsenious acid.

Of volatile substances sulphuric acid may contain:—*hydrochloric acid* (from any common salt contained in the nitrate of soda), to be proved by nitrate of silver, after having diluted the acid, silver sulphate being also very little soluble; *hydrofluoric acid*, to be proved by heating in a platinum dish covered by a glass plate coated with wax and containing scratched-in figures; *sulphurous acid*, to be proved by the decolorization of a weakly blue solution of iodized starch, or very accurately by reduction with zinc or aluminium to sulphuretted hydrogen, which is recognized by its turning lead paper brown or by colouring purple an alkaline solution of sodium nitroprusside. The *oxygen compounds of nitrogen* are nearly always present in the sulphuric acid of trade. They are recognized in the simplest manner, and with nearly as much precision as by any other test, either by the decolorization of a drop of dilute solution of indigo on heating, or by carefully pouring a solution of ferrous sulphate on the acid contained in a test-tube, so that the liquids do not get mixed. In the presence of traces of nitrous acids or of higher nitrogen oxides a brown ring will be formed at the point of contact; if more be present, the iron solution is coloured brown or black; but after some time it loses its colour again, especially if it has become warm by the reaction. *Selenium* also gives a red ring similar to that given by traces of nitrogen oxides; but the colour, instead of gradually going away, after standing for a time turns into a red precipitate at the bottom of the test-tube. Nitrous and hyponitric acids are also recognized by turning blue a solution of starch containing potassium iodide.

Probably the most sensitive of all reagents on nitric acid &c. is diphenylamine (Kopp, Ber. d. deutsch. chem. Ges. 1872, p. 284): a little of this is put in a watch-glass or a test-tube with the sulphuric acid, to which, if it is concentrated, a few drops of water are added; on stirring with a glass rod in the presence of the smallest traces of nitric acid or of other nitrogen oxides a splendid blue colour is produced, which, however, goes away after some time. Even more accurate is the reaction with carbazol, discovered by Graebe and Glaser, which with traces of nitric acid &c. yields an intense green colour which *remains*.

In order to ascertain the *gaseous impurities* of sulphuric acid quickly and certainly, Warrington uses the following process. He violently shakes up a kilogram of the acid (without dilution) in a stoppered bottle only half filled with it, so that the air contained in the bottle must be saturated with the gases dissolved in the acid. Then sulphurous acid can be detected by its decolorizing freshly prepared iodized-starch paper (obtained by dipping starch in iodine-water), and, inversely, the higher oxides of nitrogen by their turning starch-paper impregnated with potassium iodide blue. But when sulphurous acid is present in such excess that the paper turned blue by the second reaction can be decolorized again, the test will not answer. Sulphuretted hydrogen would act like sulphurous acid; both may certainly occur in traces, even along with the higher oxides of nitrogen.

For the *quantitative estimation of the foreign constituents* in a sample of sulphuric acid, separate portions must be used in estimating the volatile and the fixed compounds. For the estimation of the latter a large quantity of acid (up to 500 grms.) is diluted with water; sulphurous acid is conducted through, in order to reduce the arsenic acid to trioxide; the excess of sulphurous acid is driven off by prolonged boiling; and the liquid is saturated with sulphuretted hydrogen. The precipitate then formed may contain the sulphides of lead and arsenic, more rarely of antimony, copper, platinum, &c. These must be separated by the well-known methods of gravimetrical analysis, which are not always of a simple character. The lead can be separated almost completely beforehand by diluting the acid sufficiently; in this case mostly arsenic is looked for, which can be estimated, for instance, volumetrically by titrating its sulphide with a solution of iodine. In the filtrate from the sulphuretted-hydrogen precipitate, ferric oxide, lime, alumina, alkalies, &c. can be estimated in the usual way.

Sulphurous acid, if at all present in weighable quantities, can be estimated by a solution of iodine according to Bunsen's method. The acids of nitrogen (nitrous, hyponitric, and nitric) cannot easily be present along with sulphurous acid in sensible quantity; their quantity is very considerable, however, in certain intermediate manufacturing products ("nitrous vitriol"); and the methods for estimating it are therefore of great importance. Also in chamber-acid and in more concentrated products there is much oftener nitric acid and the nitrogen acids less rich in oxygen present than sulphurous acid; and in this case the estimation of even small quantities is sometimes of importance, because they exert a very injurious action during the concentration of the acid in platinum.

As far as *nitric oxide,* NO or N_2O_2, is concerned, Cl. A. Winkler has already proved that it is not absorbed by strong vitriol ('Untersuchungen,' 1867, p. 7). Kolb has also made experiments with acids of varying concentration (Bull. Soc. Indust. Mulh. 1872, p. 225), and has found that acid of 1·841 does not absorb even traces of NO, acid of 1·749 to 1·621 merely traces (2 to 6 milligrams to 100 grms. acid); acid of 1·426 absorbs 0·017 grm. NO; acid of 1·327, 0·020 grm. NO to 100 grms. In practice accordingly no account need be taken of nitric oxide, especially in the case of the stronger acids, since in any case it cannot be present in sufficient quantity for estimation; and the latter need only refer to the proper acids of nitrogen. Of these, again, only nitric and nitrous acid need be taken into account; hyponitric acid, in analyses where the liquids are very dilute, always behaves like a mixture of the above two acids. As far as the "chamber-crystals" are concerned, or, as they have been latterly called, nitrosulphonic acid or nitrosyl sulphate, $SO_2(OH)(NO_2)$, whose solution in sulphuric acid plays a very important part in acid-making as "nitrous vitriol," Rammelsberg and Philipp (Ber. d. deutsch. chem. Ges. 1872, p. 310) have shown that on contact with water this compound yields up $\frac{1}{4}$ of its nitrogen as NO, $\frac{5}{8}$ as NO_2H, and $\frac{1}{8}$ as NO_3H. It is not yet proved that on diluting their solution in sulphuric acid exactly the same reaction takes place; but anyhow such solution behaves towards oxidizing agents as if the compound $SO_2(OH)(NO_2)$ had with H_2O formed $SO_2(OH)_2+NO_2H$. If, however, the dilution with water takes place *before* adding the oxidizing agent, a portion of the nitrogen compounds seems to escape as NO, another to be changed into NO_3H.

First of all we must treat of the methods for estimating *nitrous and nitric acids together*, in which case the result can be calculated as N_2O_3, N_2O_5, NO_3H, &c. Frequently, for technical purposes, it is calculated as NO_3Na, because the nitrate of soda is just the raw material whose consumption is the essential thing.

Of the many methods proposed for this end I only mention those which can be applied for technical purposes.

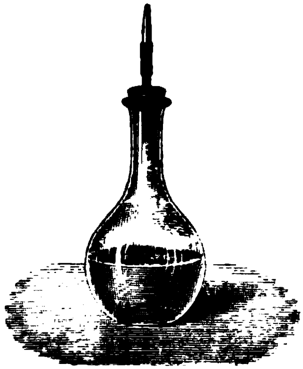
1. The method of *Pelouze*, modified by Fresenius and others, is only adapted for the estimation of nitric acid; it is, however, sometimes used for estimating a mixture of this and of nitrous acid, after the latter has been converted into nitric acid, for instance, by chlorine, potassium bichromate, permanganate, &c. Of course in the former case the excess of chlorine must be removed by boiling, which has always certain drawbacks, owing to the possibility of nitric acid being volatilized; in the two latter cases only an exactly sufficient quantity of the reagent must be added, which, especially in the case of permanganate, is easily ascertained by the change of colour.

The method of Pelouze is founded upon the fact that free nitric acid oxidizes ferrous chloride, according to the equation

$$6\,FeCl_2+2\,NO_3H+6\,HCl=3\,Fe_2Cl_6+2\,NO+4\,H_2O.$$

An exactly known quantity of ferrous chloride was taken; and by means of potassium permanganate (or, according to Fresenius, of bichromate) the excess of the ferrous salt not converted into ferric chloride by the above reaction was measured. This method had several sources of error, especially the regeneration of higher oxides of nitrogen by the nitric oxide formed in the reaction coming into contact with air. Fresenius has made the process accurate by several modifications, especially by carrying it on in a current of carbonic acid; but his apparatus is somewhat complicated for technical laboratories, and, in the author's experience, just as accurate results can be obtained with the simple apparatus represented in fig. 3.

Fig. 3.



Ferrous chloride has the drawback that, as is well known, the permanganate does not yield accurate results in the presence of muriatic acid; we therefore substitute ferrous sulphate for it. A flask of about 200 cub. centims. capacity is closed by a good cork or india-rubber stopper, through which a glass tube of about 1¼ inch length passes, cut off slanting just below the cork; its upper end is closed by a Bunsen's caoutchouc valve, viz. a piece of thick elastic tubing whose upper end is closed by a bit of solid glass rod, and which receives a sharp slit about ½ inch in length. This slit allows any gas or vapour to get out, but not to get in, since its margins close all the more tightly the more the air is rarefied within the flask; mostly the tubing in this case collapses. This simple contrivance does quite the same service as the retort-with-carbonic-acid apparatus &c. in Fresenius' plan. Into the flask an accurately weighed quantity of the finest iron wire (for instance that used for making artificial flowers) is put, say 1 grm., and pure dilute sulphuric acid is poured over it. It is preferable to throw 1 or 2 grms. of sodium bicarbonate into the flask just before putting in the cork, in order to expel the air by carbonic acid. Now the cork with its caoutchouc valve is put in, and the dissolution of the iron is promoted by gently heating; at last the liquid is boiled till it has become quite clear; then the lamp is taken away and the flask is allowed to cool, which may even be hastened by cold water. The valve prevents any air from entering the flask and oxidizing the ferrous sulphate; after cooling, such oxidation does not happen at all during the time the experiment lasts, if an excess of acid is present. The cork is then removed, the contents of the flask are diluted to about 200 cub. centims., and a solution of potassium permanganate added from a burette till the pink colour has just appeared, which can be seen best on a white ground. The value of the latter solution is found according to the following reaction:—

$$10\,FeSO_4+2\,KMnO_4+8\,SO_4H_2=5\,Fe_2(SO_4)_3+K_2SO_4+2\,MnSO_4+8\,H_2O.$$

Here we must remember that the iron wire is not chemically pure iron, but only contains, according to Fresenius, 99·6 per cent. Fe; therefore either the corresponding quantity of wire, say 1·004 grm., must be weighed at once, or the figure found must be multiplied by 0·996. The author has shown (Chem. News, xxxvi. p. 145) that this apparatus permits quite sufficiently precise estimations of nitric acid to be made; but the operation takes a very long time, unless a large excess of acid is employed—for instance, 20 per cent. SO_4H_2 by weight of the whole liquid. Otherwise the boiling must be continued till the liquid has attained this degree of concentration.

A solution of potassium permanganate is usually called seminormal if it can give up half an equivalent of oxygen (O taken as $=8$) in milligrams per cub. centim.—that is, 0·004 grm. O. Such a solution is obtained by dissolving 15·82 grms. of pure crystallized potassium permanganate in a litre of water, and is very convenient for practical use; it must, however, be checked with iron wire as above described, since even the crystallized permanganate sold as "pure" often contains 1 to 2 per cent. of impurities, which, however, do not interfere with its stability. Each cub. centim. of this solution answers at the same time to 0·028 grm. metallic iron, or 0·139 crystallized ferrous sulphate, or 0·009 N_2O_5, or 0·0105 NO_3H, or 0·01417 NO_3Na, or 0·00633 N_2O_3 (previously transformed into NO_3H). This solution changes so little even on prolonged standing, in well-closed bottles or burettes, that it is only necessary to check it about once every two months by a new experiment with metallic iron (or with oxalic acid); mostly it keeps unchanged to the last. It is much more convenient for use than the bichromate solution, with which the end of the reaction can only be ascertained by dropping on a porcelain plate covered with drops of potassium ferricyanide solution;

and since pure crystallized permanganate can be easily obtained, the objection of quickly changing, formerly justly made to the impure permanganate solution then in use, has lapsed. To be sure it must be observed that there is a known source of error in employing permanganate in the presence of hydrochloric acid (compare Fresenius' 'Quantitative Analysis,' 6th (German) edition, p. 281); but where, as in the present case, the employment of hydrochloric acid can be avoided altogether, even this reason for avoiding the use of permanganate in titrating ceases to exist.

Instead of dissolving iron wire every time with the precautions above described (which for standardizing is certainly the safest plan), in technical laboratories a solution of ferrous sulphate can very well be employed for estimations of nitric acid. It must contain so much free sulphuric acid that no further acid need be added in the subsequent operations; the presence of this free acid at the same time retards the oxidation of the iron solution so much that, at most, it need be tested for its strength only once a day. A solution of 100 grms. pure crystallized green copperas and 50 grms. of sulphuric acid in 1 litre of water is made; and for each testing a certain quantity, say 25 cub. centims., is taken out with a pipette. This is much more convenient than weighing off and dissolving iron wire on each occasion, and saves a great deal of time. First the value of 25 cub. centims. iron solution is determined by a seminormal permanganate solution, which itself has been previously standardized by means of iron wire; this can be done in a few minutes. Then another 25 cub. centims. of the iron solution is put into the flask with caoutchouc valve; a certain quantity of the liquid containing nitric acid is added, then 1 to 2 grms. of sodium bicarbonate; the flask is closed with the valve cork, heated to boiling, and the liquid boiled for some time, till it has become perfectly clear and all nitric oxide is expelled; then it is cooled and titrated back with permanganate solution as described above. Now, of course, less will be used than for the first titration; and the difference indicates for each cub. centim. of the permanganate solution a quantity of 0·009 grm. N_2O_5 &c., as mentioned above in detail. Of course the quantity of liquid containing nitric acid must be so regulated that an excess of unoxidized ferrous sulphate is left. Sometimes the boiling must be continued for a long time, up to an hour, before all nitric oxide is expelled; in very dilute liquids a very large quantity of free sulphuric acid is needed to hasten the reaction.

This method, if carefully carried out, is very accurate; for the present case (the analysis of nitrous vitriol) it has only this drawback, that the nitrous acid has first to be converted into nitric acid, and that no distinction can be made between nitrous and nitric acid.

2. *First method of F. Schulze* (*Harcourt, Siewert, &c.*).—This method is based on the conversion of nitrogen compounds into ammonia by nascent hydrogen in an alkaline solution, expelling the ammonia, and absorbing it in standard acid, which is afterwards titrated back. For the evolution of hydrogen generally a combination of zinc and iron is used; the potassic solution in Harcourt's plan is an aqueous one, in Siewert's an alcoholic one. An exact description of the method is given by Fresenius (*loc. cit.* p. 525); it is not repeated here—first because many chemists have not obtained accurate results by it, as mentioned there, and secondly because it is too troublesome for technical examinations; and this drawback need not in this case be put up with as if no better or equally good methods were in existence. It is true that Eder, in Fresenius' 'Zeitschrift f. anal. Chemie,' xvi. 309, has given a number of special precautions, which have furnished accurate results to the author as well; but the complication of the apparatus, and the tenfold longer time required for carrying out this method, are by no means recommendations of it in competition with the not less accurate ferrous-sulphate method.

3. *Second method of F. Schulze,* in which the nitric acid is estimated by the deficiency of hydrogen. On dissolving aluminium in caustic potash solution the hydrogen liberated can be measured and can be used inversely as a measure for the quantity of aluminium. But if a nitrate be present, less hydrogen is obtained, since a portion of it in the nascent state converts nitric acid into ammonia, according to the equation

$$NO_3H + 8\,H = NH_3 + 3\,H_2O.$$

This estimation can be made more accurate than that by absorbing ammonia in titrated acid, because the measuring of hydrogen can be made very exact. It is carried out in an apparatus similar to Knop's azotometer, and, together with the necessary computations, takes even more time than the former method. We shall accordingly only refer to its description in Fresenius, p. 528.

Hasenbach has proposed a process for estimating any hyponitric present along with nitrous acid. He utilizes for this purpose the property of ammonium sulphate of acting upon those two acids thus:—

$$\text{I. } 3\,NO_2+4\,NH_3=6\,H_2O+7\,N.$$
$$\text{II.. } N_2O_3+2\,NH_3=3\,H_2O+4\,N.$$

In case I. $\frac{3}{7}$ of the nitrogen liberated, in II. one half of the same equals that originally present as a nitrogen acid; by estimating this first by the ordinary processes as N_2O_3, and secondly measuring the nitrogen given off eudiometrically after addition of ammonium sulphate, it can be found which of the two acids has been present. This process, which has not been investigated more accurately, is described in the 'Berichte d. deutsch. chem. Ges.' 1874, p. 678.

Of the processes for estimating *nitrous acid* by itself, we shall describe those employing urea, bleaching-powder, potassium bichromate, and potassium permanganate. The *urea method* has been proposed by *P. Hart* (Muspratt's 'Chemistry,' ii. p. 1040), and is based on the fact that urea is decomposed by nitrous acid into carbonic acid, water, and nitrogen, thus:—

$$CON_2H_4+N_2O_3=CO_2+2\,H_2O+4\,N.$$

This reaction, as is well known, is a general one for the amides. The urea is used as nitrate, in which shape it is most easily procured perfectly pure; and one molecule in centigrams (=1·230 grm.) of it is dissolved in boiling water. The acid to be examined is added to it gradually from a burette with continual stirring; and testing is continually repeated, to ascertain if an excess be already present, by bringing a drop of the solution into contact with starch solution containing potassium iodide, of which a number of drops have been placed on a porcelain plate. As soon as a blue colour appears, no more acid is added; that already used must have contained exactly a molecule of N_2O_3 (also expressed in centigrams) =0·760 grm. N_2O_3. This number corresponds to 1·080 N_2O_5, 1·260 NO_3H, or 1·700 NO_3Na; and these figures need only be divided by the number of cub. centims. acid used in order to know how much of the above substances corresponded to 1 cub. centim. of the acid.

Crowder (Chem. News, xxiv. p. 238) obtained by this plan very discordant results; he therefore recommended as an improvement to carry out the process in one of the apparatus for estimating carbonic acid by loss of weight, and then to calculate the nitrous acid from the liberated carbonic acid and nitrogen by the equation

$$CO_2+4\,N=N_2O_3;$$
$$100 \text{ loss of weight}=76\,N_2O_3.$$

Davis (Chem. News, xxv. p. 125) declares both Crowder's modification and Hart's original process to be quite unreliable, as no two testings ever gave the same results. The author has also (*loc. cit.*) proved by figures the utter untrustworthiness of Hart's process, and the unsatisfactory results of Crowder's.

According to the research of Claus (Ber. d. deutsch. chem. Ges. 1871, p. 140) it is not allowable from the outset to rely upon the neatness of the above reaction; decompositions also take place according to the equations

$$2\,CH_4N_2O+N_2O_3=(NH_4)_2CO_3+N_4+CO_2$$
$$\text{and } 2\,CH_4N_2O+N_2O_3=CH_4N_2O+N_4+CO_2+2\,H_2O,$$

according to the conditions of working, and the nitrous acid later on not only acts upon the urea, but also upon the ammonium carbonate; especially the equation becomes quite inaccurate if strong acids are present in the free state, which on their part act upon the ammonium carbonate anyhow occurring as an intermediate stage; only then the reaction will take place exactly according to the formula $CH_4N_2O+N_2O_3=CO_2+N_4+2\,H_2O$, if a quantity of free nitric or sulphuric acid exactly equivalent to the N_2O_3 is present. Since this latter condition is impossible to realize in nitrous vitriol, it follows from the experiments of Claus that both Hart's and Crowder's process are wrong in principle.

A second process, which cannot be reproached with being too costly, has been used for many years in English factories without its author being known. It rests on the oxidation of nitrous acid by *bleaching-powder*. Of this a clear solution is made of such strength that each 10 cub. centims. of it yield 0·7 grm. of available chlorine. The solution if kept well stoppered and not exposed much to the light will keep for a long period. For each test 10 cub. centims. of it are diluted to about a litre with distilled water in a bottle of 1½ litre capacity. The nitrous vitriol is added from a burette which contains 37·4 cub. centims., divided into 100 parts. After each addition the bottle is well shaken; when the smell of chlorine is only very faint, tests are made after adding a few drops of nitrous vitriol at a time, to see whether a few drops of indigo solution are still decolorized. If the colour remains blue, the number of divisions of the burette is taken, and the percentage of N_2O_3 is obtained by dividing 100 by that number; thus at 50 measures of the burette there is

$$\frac{100}{50}=2 \text{ p. c. } N_2O_3; \text{ at 75 measures, } \frac{100}{75}=1{\cdot}33 \text{ p. c. } N_2O_3, \text{ \&c.}$$

These percentages of course refer to the *volumes* of the nitrous vitriol, and, if they are to be calculated into weights, must be divided by the specific gravity of the vitriol.

By this method, indeed, very concordant results are obtained (Davis, Chem. News, xxiv. p. 258); and it is assumed in the factories that an acid is "very good" if 60 to 70 measures of the burette are used. The relation of these figures to the percentage of real N_2O_3 is found by the following calculation. According to the reaction

$$N_2O_3+4\,Cl+3\,H_2O=2\,NO_3H+4\,HCl,$$

76 parts of nitrous acid correspond to $4\times35{\cdot}5=142$ parts of chlorine; and the 0·7 grm. chlorine in the test liquid is thus equivalent to $\frac{0{\cdot}7\times76}{142}=0{\cdot}374$ grm. N_2O_3, which must be contained in the measures of acid used out of the burette. But it cannot be assumed that this is really exactly the case, since even in a very largely dilute solution of bleach-liquor the acid running in will liberate some chlorine, which is lost. Still the bleaching-powder process is sufficiently exact for *comparative* estimation in the daily practice of factories; it gives pretty constant results, more so than the permanganate method in its former faulty state; and it can be carried out very quickly—say, in three minutes.

Davis (Chem. News, xxv. pp. 25 and 124) gives further directions for the use of this test. It is neither meant nor adapted for *small* quantities of N_2O_3, in which case the burette would have to be filled several times; for such cases the permanganate method, *properly* carried out, is incomparably preferable.

The *bichromate process* has long been known in several modifications. Mohr ('Titrirmethode,' 3rd ed. p. 236) describes it thus:—To the vitriol to be tested an excess of standard bichromate solution is added; and the remainder of bichromate is estimated by standard ferrous solution. In a simpler but ruder form the process has been used for many years in English works, nitrous acid being added from a burette to a standard solution of bichromate till the red colour had turned into a pure green. This might do for checking the practical work, but could not lay claim to any accuracy. Gerstenhöfer has specially worked out this process, and given a table showing directly the percentage of 95-per-cent. nitrate of soda in nitrous vitriol. The accuracy of his table has been disputed by Hasenbach (Ber. d. deutsch. chem. Ges. 1874, p. 678), and upheld by Büchner (ibid. p. 1665). The process is carried out in this way :—The nitrous vitriol contained in a burette is added to 20 cub. centims. of a potassium bichromate solution containing 73·8 grams in 2 litres, and therefore yielding 0·06 gram oxygen per cub. centim., or indicating

$$0·01425\ N_2O_3 = 0·031875\ NO_3Na \text{ per cub. centim.}$$

The reaction is as follows :—

$$3\,N_2O_3 + 2\,K_2Cr_2O_7 + 8\,SO_4H_2 = 6\,NO_3H + 2\,SO_4K_2 + 2\,Cr_2(SO_4)_3 + 5\,H_2O.$$

The 20 cub. centims of bichromate solution are contained in a 100-cubic-centim. flask; and the nitrous vitriol is added slowly. The liquid turns successively brown, brownish yellow, brownish green, yellowish green, and at last blue-green. The transition from yellow-green is very marked, and shows the end of the reaction. If more nitrous vitriol is added, brownish-yellow vapours appear on the top of the liquid. If it gets too warm during the work, it must be cooled by placing the flask in cold water.

Gerstenhöfer's table is the following :—

Cub. centims. of nitrous vitriol used.	Per cent. of nitric acid, 66° Tw.	Per cent. of 95-per-cent. nitrate of soda.
10	9·8	7·8
11	8·5	6·8
12	8·2	6·6
13	7·6	6·0
14	7·0	5·6
15	6·6	5·2
16	6·1	4·9
17	5·8	4·6

Cub. centims. of nitrous vitriol used.	Per cent. of nitric acid, 66° Tw.	Per cent. of 95-per-cent. nitrate of soda.
18	5·5	4·4
19	5·2	4·1
20	4·9	3·9
21	4·7	3·7
22	4·5	3·6
23	4·3	3·4
24	4·1	3·2
25	3·9	3·1
27	3·6	2·9
30	3·3	2·6

This does not agree with the equation given above, according to which 20 cub. centims. of the bichromate ought to indicate 0·6375 NO_3Na.

Among all the analytical methods founded upon the oxidation of nitrous acid, both the most convenient and the most accurate is that with *potassium permanganate,* first proposed by Feldhaus. Even for scientific purposes, there is no more accurate method for estimating nitrous acid in an acid solution than this, if other oxidizable bodies be absent.

Even nitric oxide is oxidized by this reagent, according to this equation :—

$$10\,NO + 6\,MnO_4K + 9\,SO_4H_2 = 10\,NO_3H + 3\,SO_4K_2 + 6\,SO_4Mn + 4\,H_2O.$$

Accordingly the seminormal solution of permanganate, each cub. centim. of which corresponds to 0·004 O, will show 0·005 NO for each cub. centim. Thus, on the one hand, nitric oxide can be estimated quantitatively by this reagent; on the other hand, the nitric oxide would make the estimation of nitrous acid inaccurate if it were present at the same time, which, fortunately, is not the case in sulphuric acid.

Nitrous acid itself is oxidized by permanganate, according to the equation

$$5\,N_2O_3 + 4\,MnO_4K + 6\,SO_4H_2 = 10\,NO_3H + 2\,SO_4K_2 + 4\,SO_4Mn + H_2O.$$

Here every cub. centim. of seminormal permanganate solution corresponds to 0·0095 gram N_2O_3.

The process formerly most in use was the following:—The nitrous vitriol was diluted to about 100 times its volume. Winkler asserted that this can be done without any loss of nitrogen compounds, if the nitrous vitriol be first mixed with three or four times its bulk of pure sulphuric acid, and the mixture be then carefully poured into cold water 100 or 200 times the volume of the nitrous vitriol, constantly agitating the liquid. Then permanganate is run in from a burette. It is at first decolorized rapidly, then more slowly, as the oxidation of nitrous acid in very dilute liquids is not instantaneous. The end of the reaction is assumed if the pink colour has stood for two minutes. Later on, however, it bleaches out, owing to the presence of organic substances, which gradually act upon the permanganate.

The author has shown (*l. c.*) that in this operation the figures obtained are always too low, and has directly proved the nitric acid formed in diluting the vitriol. Much better results are obtained by a modification which Professor Winkler has privately communicated to the author, according to which 5 or 10 cub. centims. of nitrous vitriol are run out of a pipette onto the bottom of a beaker containing about 500 cub. centims. of water. The liquids are at first not mixed; and when the permanganate is added, the reaction principally takes place in the lower part of the liquid, where the nitrous vitriol is very little diluted. The results thus obtained are not quite accurate yet, but sufficiently so for ordinary factory work. Still simpler is the plan of running the vitriol into a small dry beaker, and pouring about three fourths of the requisite quantity of permanganate on the top of it. At the point of contact the nitrous acid is gradually oxidized as the vitriol gets diluted. After a few minutes the liquids are mixed by shaking, and quickly as much more permanganate is added as suffices for producing a pink colour.

The permanganate method has been reproached with not giving constant results (Davis, *l. c.*), and with not proceeding according to the theoretical equation (Crowder, *l. c.*). These reproaches lapse when the process is not carried out by adding the permanganate to the vitriol, but, as is done with so many other processes, a certain volume of permanganate solution is taken, and the nitrous vitriol is run in very slowly, and with constant shaking, till the liquid is just decolorized. Here also, in the end, some time must be taken (Davis, Chem. News, xxv. p. 25), since the very dilute solution of permanganate is no longer acted upon instantaneously. This loss of time can be avoided by working at 30° to 40° C. but *no higher*. The seminormal permanganate solution ought to be diluted to from five- to tenfold. The author has proved the perfect accuracy of the permanganate method in this modification.

With this process *nitrous and nitric acid can be estimated at the same time*. First of all, the nitrous acid is estimated in the manner just described, so that the liquid at the end of the operation only contains nitric acid, sulphuric acid, and potassium and manganese sulphates. Now a certain volume of ferrous sulphate solution is added, and the total nitric acid is estimated in the manner described on p. 55, viz. by boiling with exclusion of air and titrating back with permanganate*.

Kolb takes two samples, one of which he titrates for N_2O_3 with permanganate; to the other he adds ferrous sulphate directly, and titrates back with permanganate.

In the presence of *other oxidizable substances*, such as sulphurous acid, ferrous salts, organic substances, &c., all oxidation methods are of course inexact, whether the bleaching-powder, or the bichromate, or the permanganate process. Generally those impurities are too insignificant to do any harm; and especially where large quantities of nitrous acid are present, as in the nitrous vitriol from the Gay-Lussac towers, the permanganate process is quite sufficient for the purpose of checking the course of manufacture. Of the oxidizable substances only arsenious acid sometimes occurs in sufficient quantities to affect the results sensibly, but to a small extent only, in nitrous vitriol, where it is mostly changed into arsenic acid.

A process which is free from all the drawbacks of the processes hitherto described, and which, with careful manipulation, yields perfectly accurate results in a very short time, was discovered by Walter Crum (Phil. Mag. xxx. p. 426). It has been further improved by John Watts, and has become better known by a paper of Davis's ('Chemical News,' xxxvii. p. 45). The sulphuric acid containing nitrogen acids is introduced into a graduated tube filled with mercury and standing in a mercury-trough. It is then shaken up with the mercury, which almost immediately reduces all nitrogen acids to nitric oxide, NO. The mercury inside and outside the tube is brought to the same level by lowering the tube into a depression worked in the trough; and the read-off volume of NO is calculated for N_2O_3 or N_2O_5 &c.

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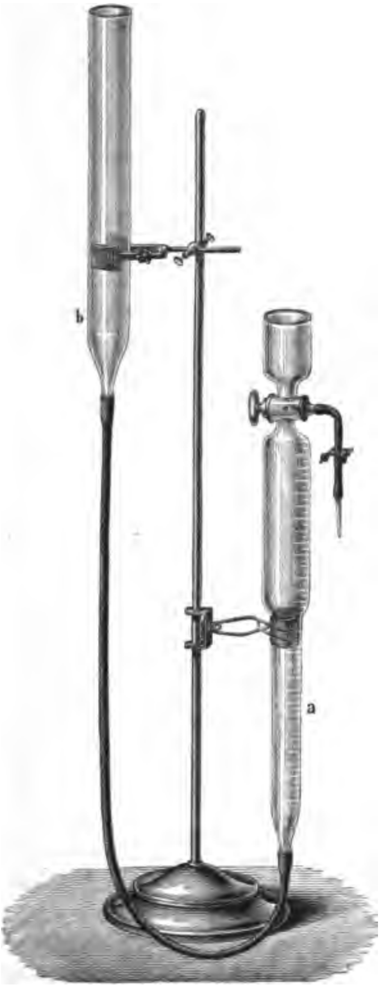
* From the nitric acid thus found that quantity is deducted which has been formed from the nitrous acid originally present. The remainder must have been present from the first as nitric acid.

The author, by a series of analyses, has proved the accuracy of this method, and has found that the presence of arsenic and of organic substances does not interfere with it (Lunge, in 'Berichte d. deutsch. chem. Ges.' xi. p. 436). However, the apparatus introduced by Davis is not very handy for technical laboratories, especially from the necessity of a mercury-trough. Davis has certainly constructed a form of trough only holding 10 lb. of mercury; but this necessitates a very short tube, and makes the shaking rather awkward; it is also troublesome to clean the tube every time. The author has therefore constructed an apparatus which contains no trough at all, in which only very little more mercury is used than is required for filling the tube itself (less than 2 lb.), in which the operator does not touch the mercury at all, and which can be readily cleaned out after each operation. This apparatus, which the author has proposed to call a "nitrometer," is represented in fig. 4.

Its principal portion is a glass tube, *a*, of a little over 50 cub. centims. capacity, divided into fifths of a cub. centim., and, for the sake of suspending it in the stand, a little narrowed in its lower half. At the bottom it tapers to fit into an elastic joint; at the top it ends in a funnel communicating with the inner part of the tube by a cock of the same kind as that employed by Winkler in his gas-burette. Its plug has one bore at right angles to its length, through which the measuring-tube communicates with the funnel, and another curved bore through which the contents of the funnel can be run off in the direction of the axis of the plug. To this a short elastic tube with a screw-clamp and a short bit of glass tubing are attached. The division of the measuring-tube, *a*, begins from the cock itself, and goes from the top downwards. The tube *a* hangs in a clamp, which can be instantaneously opened by a spring, so that the tube can be taken out. Another clamp, sliding on the same stand, carries a plain cylindrical glass tube, *b*, tapering below, of the same contents and about the same diameter as the measuring-tube. The lower ends of the two tubes are connected by a thick elastic tube. *b* slides up and down in its clamp with friction. In order to use the apparatus, *b* is placed so that its lower end is rather higher than the cock of *a*, and, the latter being opened, mercury is poured in through *b* till it has just entered the funnel of *a*. As it flows into *a* from below, it will not allow any air-bubbles to

Fig. 4.



remain in the tube. The cock is now closed; the mercury standing in the funnel is run off by the lateral bore of the cock; *b* is lowered; and the vitriol to be tested is run into the funnel by means of a fine pipette. Of course it is necessary to have an idea of the maximum quantity of NO which may be given off without expelling the mercury from the tube altogether; and the quantity of vitriol must be taken accordingly. By carefully opening the cock, the acid is run into *a* without any air being allowed to enter; in a similar way the funnel is washed out twice by means of pure concentrated sulphuric acid. It is not advisable to put more than 8 to 10 cub. centims. of acid into the apparatus; much better only 4 to 5 cub. centims. altogether are used; but in any case there must be an excess of strong sulphuric acid present. Now the tube *a* is taken out of the spring clamp and well shaken up. The evolution of gas in the case of nitrous acid commences at once—the acid taking a purple colour, in the case of nitric acid, after a minute or so. The reaction is ended by one or two minutes' violent shaking. Sometimes it takes a good while before the acid clears and the froth subsides; but mostly this is the case in a very short time; and anyhow it is necessary to wait a little, so that the apparatus may take the temperature of the air. Now by sliding *b* up or down, the level of the mercury in this tube is so placed that it is as much higher than that of *a* as corresponds to the vitriol; say, for each 7 millims. of acid 1 millim. of mercury; or else the level of the mercury is made the same in both tubes, and the height of mercury corresponding to the layer of vitriol in the tube is deducted from the barometrical pressure. The volume of the nitric oxide can be read off to $\frac{1}{50}$ cub. centim.; it is reduced by Bunsen's tables to 0° and 760 millims. mercurial pressure, and the percentage of the acid calculated from it. Each cub. centim. of NO, measured at 0° and 760 millims., corresponds to 1·343 milligr. NO, or 1·701 milligr. N_2O_3, or 2·417 milligrs. N_2O_5, or 4·521 milligrs. NO_3K, or 3·805 NO_3Na. By this process, of course, nitric and nitrous acids cannot be distinguished, but are always estimated together.

After reading off, *b* is again placed higher, the cock of *a* is opened, and thus first the nitric oxide and then the vitriol, muddy with mercuric sulphate, is driven into the funnel. When the mercury begins to enter the same as well, the cock is closed, the acid is run away through the lateral bore, and every thing is ready again for a new testing. First, the screw-clamp on the end of the glass cock is closed again, lest any fresh vitriol should run into the side tube; but it is easy to turn the plug so that the funnel during the running-in of fresh vitriol does not communicate either with the tube *a* or the lateral bore of the cock. If any sensible quantities of sulphurous acid be present, it is best to add a little powdered potassium permanganate to the vitriol.

CHAPTER III.

HISTORICAL AND GENERAL NOTES ON THE MANUFACTURE OF SULPHURIC ACID.

History of the Manufacture of Sulphuric Acid.

According to Rodwell ('Birth of Chemistry') it is very probable that sulphuric acid was already known to the ancients; but usually its first, although indistinct, mention is ascribed to the Arab Geber, who speaks of the "spirit" which can be expelled from alum and which possesses solvent powers. Others give this honour to the Persian alchemist Abu-Bekr-Alrhases, who is said to have died in 940. Vincentius de Beauvais (about 1250) alludes to it; and Albertus Magnus (1193–1280) speaks of a *spiritus vitrioli Romani*, which can only have been sulphuric acid; his "sulphur philosophorum" is the same thing.

With all distinctness Basilius Valentinus, in his 'Revelation of the Hidden Manipulations,' describes its preparation from calcined copperas and silica; and in his 'Triumphal Car of Antimony,' its preparation by burning sulphur with saltpetre (Kopp, 'Geschichte der Chemie,' iii. p. 303); but he took the two for different substances.

Gerhard Dornæus (1570) described its properties accurately; Libavius (1595) recognized the identity of the acids from different processes of preparation; the same was done by Angelus Sala (1613), who pointed out the fact, which had sunk into oblivion since Basilius, that sulphuric acid can be obtained by burning sulphur in moist vessels (of course with access of air); after that time it was prepared by the apothecaries in this way. An essential improvement, viz. the addition of a little saltpetre, was introduced in 1666 by Nicolas le Fèvre and Nicolas Lémery. This caused a sort of manufacture of vitriol which is said to have been introduced into England by Cornelius Drebbel: this only is certain—that a quack doctor of the name of Ward first carried on sulphuric-acid making on a large scale at Richmond near London, probably a little before 1740. Ward employed large glass vessels up to 66 gallons capacity, which stood in two rows in a sand-bath, and which were provided with horizontally projecting necks; at the bottom they contained a little water. In each neck there was an earthenware pot, and on this a small red-hot iron dish, into which a mixture of one part saltpetre and eight parts of brimstone were put; then the neck of the bottle was closed with a wooden plug; on the combustion being finished, fresh air was allowed to enter the vessel, and the operation was repeated till the acid had become strong enough to pay for concentrating in glass retorts.

Ward called the product "oil of vitriol made by the bell" (already Basilius Valentinus had used the expression "per campanam" in this sense), in order to distinguish the spirit of vitriol made from brimstone from that distilled from copperas, the latter having been made on a kind of manufacturing scale in England previously: an exact description of this is given by J. C. Bernhardt in his 'Chemische Versuche und Erfahrungen,' 1755. Ward's process, troublesome as it is, reduced the price of the acid from 2*s*. 6*d*. per ounce (the price of the acid from copperas or from burning brimstone under a moist glass jar) to 2*s*. per lb.

An extremely important improvement in this process was the introduction of the *lead chambers*, which by general consent is ascribed to a Dr. Roebuck of Birmingham, who in 1746 erected such a chamber 6 feet square, and in 1749, in partnership with Mr. Garbett, built a factory, founded thereon, at Prestonpans in Scotland, in order to supply acid for the bleaching of linen. The mixture of brimstone and saltpetre in the above proportion was put into small iron waggons which were run into the chamber on a railway; the chamber was closed, and the process carried on intermittently in this way.

Soon other works followed at Dowles in Worcestershire, where the chambers were already made 10 feet square; in 1772 there was a factory erected in London with 71 cylindrical lead chambers, each 6 feet diameter and 6 feet high. In 1797 there were already six or eight works in Glasgow alone. According to the statements given in Mactear's 'Report of the Alkali and Bleaching-Powder Manufacture in the Glasgow District' (p. 8), the acid at that time cost the Glasgow manufacturers £32 per ton, and was sold at £54. At Radcliffe, near Manchester, it cost, in 1799, £21 10*s*. per ton, without interest on capital. In the latter place there were six chambers 12 feet long, 12 feet wide, and 10 feet high, with roofs like those of houses, and valves opened between each operation; on their bottom there were 8 or 9 inches of water; every four hours there was burnt in each chamber a mixture of 1 lb. saltpetre and 7 lb. brimstone on iron shelves, of which each chamber contained four, 4 inches distant from one another. The shelves were made of very thin iron, in order to get heated very quickly, and rested on iron frames, by means of which they could be slid in and out; a quarter of an hour before each operation the valves and doors were opened in order to allow air to enter. Thus, weekly, 1386 lb. of brimstone and 198 lb. of saltpetre were burnt, yielding 1800 lb. of oil of vitriol—that is, 130 per cent. of the sulphur with a consumption of 14·28 per cent. saltpetre on the same. In six weeks the strength of the acid only attained 1·250 sp. gr.; it was then run off and concentrated up to 1·375 sp. gr., in which state it was used and sold. At Prestonpans, in 1800, only a yield of 111 per cent. on the sulphur was attained, with a consumption of 13 per cent. saltpetre on the brimstone; in 1813 there were in that place 108 chambers of 14 feet length, 10 feet height, and 4½ feet width. In 1805 there existed at Burntisland a factory with 360 chambers of a capacity of 19 cubic feet each.

In the mean time the first lead chamber in France had been erected at Rouen by Holker in 1766. In 1774, in that place, on the advice of De la Follie, an important improvement was introduced, viz. the introduction of steam into the chambers during the combustion of brimstone. In 1793 Clément and Desormes showed that the acid-chambers can be fed by a *continuous* current of air, by which a great deal of saltpetre could be saved. They showed that the oxidation of sulphurous acid takes place to the extent of nine tenths at the expense of atmospheric oxygen, and that the saltpetre only plays the part of intermediary between the air and the sulphurous acid. By this the modern theory of the essence of the sulphuric-acid-making process was established; but it took a remarkably long time before the difficulties were overcome which stood in the way of introducing the continuous system into practice. Usually the introduction of the continuous burning of brimstone is ascribed to Jean Holker (a grandson of the first Holker), in 1810; but, according to Mactear, a continuous system had been introduced at St. Rollox, at least partially, already in 1807: steam was first introduced there in 1813 or 1814.

In Germany the first lead chambers seem to have been those at Ringkuhl, near Cassel. One of the oldest chambers was that erected by a Dr. Richard at Potschappel near Dresden in 1820; as he had no plumber at his disposal, he had to solder the chamber himself with soft solder and a smoothing-iron (Bode, in his translation of H. A. Smith's 'Sulphuric Acid Manufacture,' p. 96). This chamber was still charged intermittently, 100 lb. of brimstone yielding only 150 lb. of vitriol. It must therefore be said that the industry of vitriol-making was very late in gaining a footing in Germany.

Kestner, of Thann in Alsace, was the first to collect the products of condensation at the chamber-sides in order to regulate the working of the chambers thereby; this innovation was at once considered of such importance that Kestner was called to Glasgow in order to introduce his plan into Tennant's works.

At last, in 1827, Gay-Lussac's condensing-apparatus for the nitre-gas escaping from the chambers was invented; in Glasgow this apparatus was erected in 1844. But we have now come so near the present time that we may conclude the historical part of our task.

General Principles of the Manufacture of Sulphuric Acid.

Sulphuric acid can be obtained on a large scale in one of two ways—viz., first, by burning brimstone or metallic sulphides into sulphurous acid and further oxidizing the latter, or, secondly, by decomposing natural or artificially prepared sulphates. The latter process, apart from several proposals so far not carried out practically, only serves for making fuming oil of vitriol, which will be treated of hereafter; by far the greater portion of sulphuric acid is obtained by the former process, which will occupy us in the first instance. We shall, at first, only describe those apparatus and processes which actually serve for manufacturing on a large scale; and we shall close by mentioning the alterations which have merely remained as proposals, as well as the processes founded on totally new principles.

By the *combustion of sulphur*, either free (as brimstone) or combined with metals, *sulphurous acid* (sulphur dioxide, SO_2) is always formed at first. Brimstone ignites in the air at a temperature rather below 300° C.; and when once it has begun to burn, the heat generated suffices to raise the whole of the sulphur to the point of ignition, provided that sufficient air be present. A series of metallic sulphides behaves similarly; the most important of these for our purpose is the iron bisulphide, FeS_2; but here special precautions must be taken, so that the whole mass may be completely burnt (roasted). In both cases, along with sulphur dioxide, SO_2, a little trioxide (sulphuric anhydride), SO_3, is always formed, and, in the presence of water or steam, also sulphuric acid, SO_4H_2, more or less diluted with water. Moreover an aqueous solution of sulphurous acid in contact with air gradually changes into sulphuric acid. In both cases it is, of course, the oxygen of the air which converts the SO_2 into SO_3 or SO_4H_2; but this reaction at the ordinary or only a moderately high temperature goes on far too slowly to be applicable for technical purposes. There are two ways of increasing the affinity between SO_2 and O, either in the presence or in the absence of H_2O. One way (which can be employed also in the absence of water or steam) is the employment of porous substances, which condense both the oxygen and the sulphurous acid; the affinity between the molecules thus brought much closer together is increased to such an extent that ultimately they combine chemically, at least partially, and yield sulphuric anhydride or hydrate, according to whether water is present or absent. As such porous substances, pumice, burnt clay, chromium sesquioxide, iron peroxide, cupric oxide, even cotton-wool, have been recommended. The action of these substances, however, which must always be increased by higher temperatures, is so incomplete that they have found no technical application. The case stands rather better with platinum, which, as is well known, exercises an extraordinarily strong condensing power upon gases at its surface, so that, for instance, hydrogen and oxygen can be brought thereby to combine at the ordinary temperature. The more finely divided the platinum is, the larger, therefore, its surface for a certain weight, the more energetically it acts in that way; and the best results have been obtained with platinized pumice and asbestos. This will be explained in detail with the fuming oil of vitriol; here it may suffice to say that platinum, even in its most finely divided form, cannot form the foundation of a real manufacture of sulphuric acid, and that the only successful proposal for utilizing it starts from already manufactured acid, in order to make anhydride from it.

The second way of making the oxygen of the air better adapted for combining with sulphurous acid is the only one actually employed in practice. It is founded on the property of the acids of nitrogen of decomposing, in the presence of water and sulphurous acid, to nitric oxide and sulphuric acid, and upon the property of nitric oxide of re-forming higher nitrogen oxides in the presence of oxygen (or air). This process will be explained in detail when we treat of the theory of the formation of sulphuric acid.

We have just seen that the reaction between nitrogen acids and sulphurous acids only goes on in the presence of water; and we must add at once that, in practice, much more water is needed than suffices for the formation of SO_4H_2; the sulphuric acid formed is therefore always *dilute*, and must be *concentrated* for most purposes.

For some purposes the acid must also be deprived of certain foreign substances which get into it from the raw materials and the apparatus; and in that case the sulphuric acid has to be *purified*.

Thus our subject subdivides itself into the following headings:—

1. *The generation of sulphurous acid.* Since the respective processes differ very much, both as to apparatus and as to the way of proceeding, we have to distinguish between (*a*) sulphurous acid from brimstone, (*b*) from metallic sulphides.

2. *The conversion of sulphurous acid into sulphuric acid,* which is always done in the so-called lead chambers, where also the introduction of nitric acid and steam, and the recovery of the nitre-gas carried away by the draught, will be described.

3. The *purification.*

4. The *concentration* of vitriol.

5. The *utilization of the by-products.*

All this will be preceded by an examination of the *raw materials* of the sulphuric-acid manufacture.

CHAPTER IV.

THE RAW MATERIALS OF THE SULPHURIC-ACID MANUFACTURE.

1. *Brimstone.*

ALTHOUGH, as we shall see below, brimstone has been almost entirely given up as a raw material for vitriol-making in Europe (principally because its price is much higher than that of the sulphur in pyrites), yet the export from Sicily has almost constantly been increasing, as is shown by the following table (from Hasenclever, in Hofmann's Report, 1873, vol. i. p. 155) :—

	tons.
1862	143323
1863	147035
1864	139841
1865	138232
1866	179110
1867	192320
1868	172387
1869	170141
1870	172751
1871	171236

In 1875 there were exported from the three principal ports of Sicily 217976 tons of brimstone, of which 50195 went to England, 40464 to France, and 26139 to America; in 1877, altogether 231743 tons, viz. 51818 to England, 38440 to France, 42589 to America, 98896 to Italy and other countries.

The cause of this large exportation is partly the increased manufacture of gunpowder—mostly, however, the enormous consumption of sulphur in the vineyards of France, Italy, and Spain for combating the *Oidium*. It was, indeed, especially the rise in the price of brimstone consequent upon the demand for it from the wine-countries, which has driven it out of the vitriol works, after (at a former period) an *arbitrary* rise in the price of brimstone had led to the first use of pyrites in those works.

Looking at the great advantages which the manufacture from brimstone offers over that from pyrites, it might be thought that perhaps at a future time, either when another remedy for the disease of the vine is found, or when the many other known sulphur-beds are properly worked, the price of brimstone would fall sufficiently to allow its re-introduction into chemical works; but this is hardly likely (except under special circumstances, such as exist, for instance, in America), since the cupreous pyrites has come into the market, in which the copper always remains the main thing, and whose sulphur will always be cheaper than brimstone, because it *must* be driven off before the copper can be obtained.

Sulphur (the principal constituent of brimstone) is an element whose atomic weight is now assumed to be 32. It is very brittle; its hardness is from 1·5 to 2·5 of the ordinary mineralogical scale; its specific gravity is 2·0454. As usually occurring, it is semi-transparent at the edges and of the well-known bright yellow colour, which darkens with an increase of temperature; at $-50°$ it is nearly devoid of colour. Its taste and smell are very slight. It does not conduct electricity, but itself becomes electric by friction; and it is therefore difficult to powder finely, as it adheres to the mortar and pestle.

Sulphur melts at 111°·5 C., and forms a thin, light-yellow liquid, which, on being more strongly heated, becomes darker and thicker; at 250° to 260° C. it is nearly black, and so viscid that it does not run out when the vessel is upset; at a still higher temperature it becomes thinner again, keeping its brown colour; and at 440° C. it boils, forming a brownish-red vapour; but it begins to volatilize before boiling.

Sulphur exists in different allotropic condition. That occurring in nature often appears in rhombic crystals, mostly pointed rhombic octahedra, whose physical properties have been described above; this α-modification is also obtained by crystallizing sulphur from its solution in carbon bisulphide. The β-modification is obtained by slowly cooling melted sulphur, and pouring off the liquid portion when another portion has crystallized; it consists of long thin oblique rhombic prisms, belonging to the monoclinohedric system, of a brownish-yellow colour, transparent, spec. grav. 1·982; they gradually pass over into the α-modification, completely so after a few days, even at the ordinary temperature—suddenly by shaking or scratching; the colour then becomes light yellow; and the crystals lose their transparency, but remain as pseudomorphs of the α-sulphur. The sulphur in rolls consists, when fresh, of β-sulphur—after a short time, of α-sulphur. When sulphur has been heated up to the point of viscosity, and is then poured into very cold water, the γ-modification is formed, viz. amorphous, soft, tough, reddish-brown sulphur, of 1·957 spec. grav.; this also is gradually converted into a-sulphur; but it takes some time before this conversion is complete. The tough state lasts very much longer if resinous substance, iodine, &c. are mixed with the sulphur, even in very small quantity. This modification is partly contained in the "flowers" of sulphur.

Heated in the air to 260° C., sulphur inflames and burns with a purplish-blue flame, forming sulphur-dioxide (SO_2), and giving out 2221 metrical units of heat. Sulphur is insoluble in water, a very little soluble in alcohol, rather more so in essential oils, but easily soluble (excepting the γ-modification) in bisulphide of carbon and in chloride of sulphur.

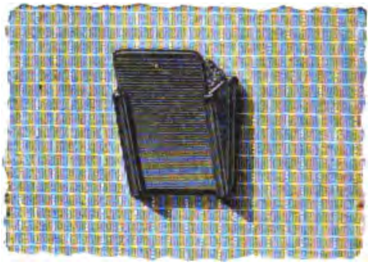
Sulphur occurs in nature in very large quantities, both in the free state as brimstone, and in combination with other bodies as sulphides and sulphates. Deposits of brimstone are forming at the present time in volcanic countries by the decomposition of sulphuretted hydrogen and of sulphurous acid. But of far more importance are the beds of brimstone deposited in former geological periods. The most important of all are those of Sicily, in the Chalk; next, those in the Romagna and in other parts of Italy. The Sicilian brimstone-industry is described in detail by Angelo Barbaglia in Hofmann's Official Report on the Vienna Exhibition, i. p. 144, and by Parodi (Berichte d. deutsch. chem. Ges. 1874, p. 358). According to the latter, the disposable stock of brimstone in Sicily is said to amount to ten millions of tons; so that it would be exhausted about 1950. Other calculations give more than twice that figure. The apparatus for melting the sulphur out of the "sulphur-earth" in Sicily is also described by Barbaglia; we will only mention that the melting has lately been very successfully effected by high-pressure steam, in apparatus quite similar to that of Schaffner, which will be described with the recovery of sulphur from alkali waste.

Other beds of sulphur, but of inconsiderable extent, have long been known in Croatia, in Upper Silesia, in Poland, especially at Swoscowice near Cracow. The sulphur is here contained in a marl, of which annually 20,000 tons are got. Formerly it was extracted by distillation; latterly this has been done partly by melting in a Schaffner's apparatus (see above), partly by extraction with carbon bisulphide. A few beds of sulphur are worked in Spain, others near Mossul in Mesopotamia, near Cairo, in Tunis, China, Japan, Quito, Mexico, &c. The more important sulphur-mines worked or discovered during the last few years are:—those of Djemsah and Ranga, on the coast of the Red Sea, where the "Compagnie Soufrière" is said to get 300 tons monthly; in Iceland, where there is said to be far more brimstone than in Sicily; on the island of Saba, where 60 per cent. sulphur is contained in the gypsum, and which is claimed as the richest source for brimstone in the world (Kingzett, in 'Iron,' vol. iii. p. 610); in the Sierra Nevada (U. S. A.) also most extensive sulphur-mines are said to exist. Somehow, none of these grand mines have made any sensible impression upon the sulphur trade as yet.

The *refining* of sulphur does not belong to our task; we shall only mention that the apparatus of Dujardin, described in the modern text-books, is still that mostly used in practice. In Belgium, in 1871, more than 5280 tons of refined sulphur were obtained.

Apart from the brimstone existing in the free state, and only mechanically mixed with earthy impurities, a certain quantity of sulphur is obtained by the *distillation of pyrites*. This, however, pays in very few places, except under special circumstances—for instance, at the works of T. D. Starck in Bohemia, which supply nearly all the fuming oil of vitriol, and where the distillation of pyrites is practised in order to obtain a material for copperas-making. Between 1863 and 1872, 2440 tons of sulphur were thus made. The distillation takes place in earthenware tubes 3 ft. 3 in. long, 5 in. high, and 5½ in. wide, quite open at the back, and in front narrowed to an opening of ¾ in. diameter; they are glazed with common salt; and three tiers of seven tubes each are placed in each furnace. For each tube there is a small receiver of sheet-iron half filled with water, and attached to the tapering end of the tube. The charge of pyrites is put into the open end; a slanting piece of sheet-iron is placed in front; and the opening is closed with sand or pyrites cinders, as shown in fig. 5.

Fig. 5.



Here only one third of the sulphur contained in the pyrites is gained; but in Sweden half (?) of the sulphur is said to be obtained in a furnace built similar to a lime-kiln, and continued at the top in a wooden chimney serving as condensing space. The kiln, having been first made red-hot, is charged with pyrites, of which one portion is burned whilst the other portion volatilizes and is condensed at the top. The work is carried on continuously, fresh pyrites being from time to time introduced through an opening near the top, and the cinders being removed at the bottom.

P. W. Hofmann (Dingl. Journ. ccxx. p. 232) has made a proposal for utilizing the sulphur of the pyrites smalls, which are obtained in enormous quantities at the pyrites-mines and are very difficult to sell. If sulphurous acid is conducted over red-hot calcium sulphide (from alkali-waste), it is at first completely absorbed; afterwards sulphur distils over, and the calcium sulphide is transformed into sulphate. The latter, by conducting ordinary coal-gas over it in a red-hot state, or by mixing it with coal and igniting, is reconverted into sulphide, which can be used over again. Hofmann proposes to burn the pyrites smalls at the mines, to obtain their sulphur by means of calcium sulphide in a state fit for sale, to treat the cinders by a process to be described in the 16th Chapter for zinc chloride and sodium sulphate, and to work the residue for pig-iron in a blast-furnace. This proposal has not found any application in practice, and is not likely to do so, since the burning of pyrites dust by the new shelf-furnace is equally advantageous for acid-making with that of lump ore.

Gerlach (German Patent 229, 3rd July, 1877) proposes to obtain sulphur from sulphur-ores, and especially from the spent oxides of gas-works, by heating them in iron or fireclay retorts whilst at the same time superheated steam is passed through. The sulphur is said to distil very rapidly.

According to a French patent of the Société de St. Gobain (No. 107,820, 28th April, 1875), on the top shelf of an ordinary shelf burner for pyrites smalls (see Chapter VI.) a fireclay retort is to be placed, in which the pyrites is first deprived, by distillation, of a portion of its sulphur, which is collected in the well-known condensing-chambers as flowers of sulphur. After some time the partially desulphurized pyrites is let down to the next lower shelf, and so forth lower down. Here the remainder of the sulphur burns, and the gas goes into acid-chambers, whilst its heat causes the distillation of further portions of pyrites in the retort. This process does not answer: the flowers of sulphur obtained are very acid; and both the burner and the chambers work very badly.

In trade, three *qualities* of Sicilian brimstone are distinguished. The "firsts" consist of large, shining pieces, of amber-colour, and are rarely used for vitriol-making; the "seconds" are not so shining, but still purely yellow; the "thirds" are of a dirtier colour; and both the latter qualities, as they arrive in England, contain much powder. They are generally very little contaminated with impurities, and often only leave ½ per cent. of ash, very rarely more than 2 per cent.

The only and entirely sufficient technical assay of brimstone is that by burning a weighed quantity in a small porcelain capsule, and estimating the quantity of ash left behind.

2. *Pyrites.*

Only a comparatively very small quantity of sulphuric acid is still made from brimstone. Already, in 1868, Mactear stated that in the preceding year, of a total consumption of 160,000 tons of sulphur, only 10,000 to 20,000 tons had been brimstone, the remainder being furnished by pyrites, of which 375,000 tons had been consumed. This proportion between brimstone and pyrites is probably even more unfavourable for the former to-day, as far as Great Britain is concerned. Only a few small factories make brimstone-acid for special purposes requiring a purer vitriol; but all alkali, all superphosphate, and even the greater part of oil of vitriol (sold as such) are made from pyrites.

In Germany, as well, brimstone has been almost entirely abolished as a raw material for vitriol-making. But in the United States, whose chemical production certainly is very insignificant in comparison with that of Europe, brimstone is still exclusively employed for that purpose, partly imported from Sicily, partly found in several of the States and territories of the Union (Nevada, Utah, Wyoming, Montana). Although America possesses large stocks of pyrites, the enormous distances of the places where it occurs from the manufacturing centres do not allow of its application. Several manufacturers who had tried to use pyrites have given it up again (Goldschmidt, 'Austrian Report on the Philadelphia Exhibition,' vii. p. 5). Even the large and widely-found beds of cupreous pyrites (mentioned *l. c.* p. 11) at Vermont, Missouri, Lake Superior, Tennessee, Virginia, &c. have not found any similar use to that of the Spanish and Norwegian pyrites in Europe; but this can only be a question of time.

The first application of pyrites for sulphuric-acid-making is generally ascribed to a Mr. Hill, of Deptford, who in 1818 took out a patent for it. In France, Clément-Desormes seems to have made the first proposals and experiments in that way. His trials did not, however, succeed, because he believed it necessary to increase the combustibility of pyrites by an addition of coal. This is both unnecessary, with properly constructed kilns, and very injurious to the process, from the carbonic acid getting into the chambers. A great difficulty was experienced in lighting the kilns. So long as it was attempted to do this from below, like an ordinary fire, the thing would not work. According to communications from Mr. Todd (Government Inspector of Alkali Works for the Newcastle district), a workman of his father's in Cornwall, in 1830, accidentally discovered the way of lighting the kilns from the top, such as is practised to this day. Generally, however, the principal merit of introducing pyrites is ascribed to Messrs. Perret and Son, of Chessy, who were led to it by the necessity of desulphurizing their cupreous pyrites previously to getting the copper, and of condensing the gas evolved. There was no question then of supplanting the Sicilian sulphur generally. Perret and Son, with the greatest care, searched into all the conditions necessary for a proper combustion of the ore; and to them the honour is due of having overcome all the difficulties opposed to the solution of this problem, and of having rendered the process technically useful. Already in 1833 they had burnt iron-pyrites successfully; and in a patent dated November 20th, 1835, they described their process, to which their partner, Olivier, is said to have given the first impulse. In 1837, Messrs. Wehrle and Braun, in Bohemia, used pyrites for generating sulphurous acid (Otto, 'Lehrbuch der Chemie,' 4th ed. iii. 1, p. 545); but, according to Bauer (*l. c.* p. 6), I. Brem had introduced this process into Austria already in 1833—that is, at the same time as Perret.

These trials at making vitriol from pyrites possessed, however, only local interest; and probably for a long time no general attempt to do away with Sicilian brimstone would have been made, but for the Neapolitan Government, in 1838, being induced to grant a monopoly for the exportation of Sicilian sulphur to the Marseilles firm of Taix and Co. This firm at once raised the price of brimstone from £5 to £14 per ton, and thus would have given a fatal blow to the manufacture of artificial soda ash, just then beginning to take a firm hold, if no other source of sulphur had been known in the world, and if such an unnatural measure could have been carried out at all. But the attempt came too late—just after Perret and Son had proved that the pyrites occurring in most industrial countries could be used for vitriol-making without any difficulty. The result was to be foreseen. Once the discovery of a new source of sulphur had become a matter of necessity, there were, within twelve months from the rise in the price of brimstone, fifteen patents taken out in England for burning pyrites for the purpose of making sulphurous acid, and even a larger number for making sulphur from pyrites, gypsum, &c.

According to Muspratt's 'Chemistry' (vol. ii. p. 1023), Dr. Thomas Thomson was the first in England to point to pyrites in this crisis; but most probably many others at the same time turned to it. So much is proved—that Thomas Farmer, of London, was the first in England who employed pyrites on a large scale (in 1839) for the manufacture of sulphuric acid (Hofmann, 'Report by the Juries, International Exhibition, 1862, Class II. Section A,' p. 12).

In Germany the Oker smelting-works, at the Rammelsberg, near

Goslar, seem to have been the first who calcined the local ore in such a way as to convert the sulphurous acid given off into sulphuric acid in acid-chambers (in 1840); and other smelting-works, such as those at Freiberg, followed their example. In these cases the reasons were, not only that at a comparatively small expense sulphuric acid could be obtained as a by-product from the sulphurous acid otherwise lost, but also that the acid fumes destroyed the vegetation of a large district round the works, and that means had to be taken for preventing this, apart from any consideration of profit.

The Sicilian-brimstone monopoly certainly did not last long; diplomatic pressure on the part of England soon led to its abolition; and with the lowering of the price of brimstone most works at first returned to its employment. But the ice was now broken; the conviction had been gained that it was possible to make acid without Sicilian brimstone; the owners of pyrites mines took pains to advance the use of pyrites by low prices; and thus, in the course of the next twenty years, gradually, but steadily, brimstone was more and more driven from its place in sulphuric-acid-making, in proportion as, on the one hand, it became dearer from the causes above mentioned (disease of the vines &c.), and as more pyrites mines were opened out.

The decisive point in favour of the use of pyrites was this, that more and more *cupreous pyrites* came into the market, from Spain especially, but also from other countries. These had at any rate to be burnt and their sulphur expelled before they could be worked for copper. Already with Perret and Son this had been the stimulus for their efforts; but this has been done on a much more colossal scale in consequence of the opening out of the cupreous-pyrites mines in the south of Spain, in Portugal, and in Norway. In England, now-a-days, iron-pyrites is all but out of the field, and has been supplanted by cupreous pyrites. This has been the case to a smaller extent in France and Germany up to the last few years, because these countries possess sufficient mines of rich pyrites, which in England are not numerous; but even in those countries more and more cupreous pyrites is coming into use. In 1867 pyrites had almost entirely supplanted brimstone in France as a raw material for acid-making in the large industrial centres ('Rapport du Jury International, Expos. Univ. de 1867,' vol. vii. p. 19). In Germany this state was brought about somewhat later, but quite as completely. Only during the feverish years 1871 to 1873, when the price of pyrites had risen very high, a few factories in Hanover, at Hamburg, and Stettin temporarily returned to the use of brimstone (Hasenclever, *l. c.* p. 155); but with lower prices of pyrites this has been given up again.

Thus, starting from the use of iron-pyrites, that of cupreous pyrites has followed; and to this was added the employment of other sulphurous ores, and of the intermediate products of smelting—for instance, copper-regulus (" coarse metal ") at Mansfeld and Swansea. At the present time the Freiberg works work even poor lead-matts with about 22 per cent. of sulphur, which a few years ago was thought impossible (Bode, 'Beiträge zur Theorie und Praxis der Schwefelsäurefabrikation,' 1872, p. 1). We shall elsewhere describe the application of other sulphur-ores apart from pyrites proper.

An idea of the extension which the use of pyrites has obtained is given by the following Tables (p. 86, compiled from Hunt's 'Mineral Statistics') of the importation of pyrites and brimstone into Great Britain. (The brimstone, of course, mostly serves for other purposes than acid-making, such as gunpowder &c.)

The following Table is given by Hasenclever (*l. c.* p. 158) :—

Amount (in tons) of Pyrites produced in the under-mentioned Mining Districts.

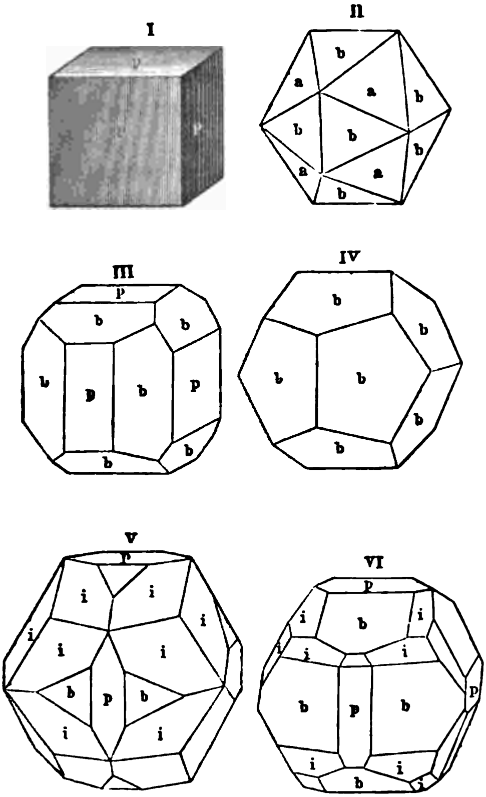
	Belgium.	Chessy and Sain-Bel, near Lyons.	Goslar.	Siegen.	All other Prussian mines.
1862	...	45,973	...	14,850	7461
1863	36,244	59,699	...	28,765	5934
1864	28,956	61,103	...	29,115	3437
1865	31,818	63,538	...	34,060	4187
1866	55,004	65,222	...	50,875	4302
1867	41,298	75,653	1599	71,835	4756
1868	37,933	75,656	2635	90,100	3953
1869	31,670	91,020	2689	64,789	6394
1870	28,665	63,464	3225	92,048	3191
1871	42,272	68,797	3324	110,432	4574
1872	40,932	99,000	3640	144,745	964
1873	...	127,000	1217	123,172	3748

To the British importations must be added the production of pyrites in Great Britain itself, which, according to Hunt's 'Mineral Statistics,' in 1874, amounted to 56,208 tons.

	PYRITES FROM								BRIMSTONE FROM
	Norway.	Germany.	Belgium.	Portugal.	Spain.	Italy.	Other countries.	Total.	Sicily.
1862 ……	4975	6817	9860	53296	33717	……	2187	110852	54200
1863 ……	6736	15409	12059	109180	33213	……	2628	179225	43060
1864 ……	16087	12751	7069	118489	15529	……	1065	170990	40420
1865 ……	22229	14727	2121	137787	16393	……	369	193626	49840
1866 ……	38262	21574	4006	165993	11910	1226	1625	244596	62850
1867 ……	77895	34592	2299	105556	50222	……	2134	272698	59270
1868 ……	63007	41559	……	75883	47458	794	1019	229720	64080
1869 ……	63091	13983	……	140805	99648	……	2420	319947	51580
1870 ……	67464	14917	……	174459	150996	……	3676	411512	54120
1871 ……	74416	12809	……	120573	242163	……	4581	454542	
1872 ……	71665	5682	……	180329	257429	……	2521	517626	
1873 ……	67462	……	……	199559	246692	……	6634	520347	
1874 ……	41004	……	……	162609	294117	……	907	498637	

What is called *pyrites* or *iron-pyrites*, in a technical sense, is hardly ever pure iron bisulphide, FeS_2, but either a mixture of this with gangue, or more frequently at the same time with other sulphuretted ores, as shown by numerous analyses. The iron bisulphide may be present either as iron-pyrites proper or as marcasite. The iron-pyrites proper crystallizes in the regular system, with parallel hemihedry, proved even on the faces of the cube by striation (fig. 6).

Fig. 6.

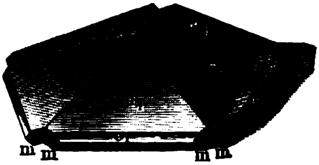


Besides the cube (I), the octahedron, *a* (II), is frequently found, often modified by the pyritohedron, *b* (III), and, if both are equally developed, forming the icosahedron (II). The combined forms IV, V, and VI, as well as twin crystals, frequently occur. The crystals are often well developed; but in the pyrites used on the large scale they are mostly quite indistinct. The colour of pure pyrites is greyish yellow, and easily distinguished from that of copper-pyrites. The microcrystalline pyrites of trade often shows other colours, even a slate-grey; the powder is brownish black. Its cleavage parallel to the faces of the cube is not very pronounced; the fracture is conchoidal or irregular. Hardness 6 to 6½, specific gravity 4·83 to 5·2. Pure FeS_2 contains 46·67 per cent. of iron and 53·33 per cent. of sulphur.

According to Mène, the pyrites from volcanic formations contains no water, but that from sedimentary strata both water and clay. Among the first he classes the yellow octahedrical pyrites, which is stable in the air; among the latter the grey cubical pyrites, which is easily transformed into ferric sulphate (Compt. Rend. 29th April, 1867).

Marcasite crystallizes in the rhombic system, in rhombical prisms $M = 106^\circ\ 2'$ with longitudinal faces $l = 100^\circ$ and r, and the end face P inclined to r at an angle of $158^\circ\ 20'$. They frequently occur in twin crystals, partially united along one of the faces M, also in triplets and quadruplets, &c. (fig. 7), in fibrous, bulbous, &c. varieties; cleavage indistinct; hardness 6 to 6·5; specific gravity 4·65 to 4·88; colour grey to yellow or greenish yellow, lighter than iron-pyrites proper; powder greenish dark grey. Marcasite is most frequently found in bituminous slate and coal, and decays even more quickly than pyrites, with formation of copperas basic ferric sulphate.

Fig. 7.



In the ores of commerce there is often present, mixed with FeS_2, *magnetic pyrites* of the formula Fe_7S_8, with 60·5 iron and 39·5 sulphur; colour between brass-yellow and copper-red; hardness 3·5 to 4·5; specific gravity 4·4 to 4·7.

The *copper-pyrites* so often mixed with iron-pyrites is distinguished from it by its colour, yellow as brass, sometimes as gold; this colour modifies that of the iron-pyrites according to the degree of admixture. It crystallizes in the tetragonal system, but in the ores which concern us always occurs in a microcrystalline form. Its hardness is 3·5 to 4·0, specific gravity 4·1 to 4·3. Pure copper-pyrites of the formula $FeCuS_2$ should contain 30·53 per cent. iron, 34·58 per cent. copper, and 34·88 per cent. sulphur; but the ores serving for the manufacture of sulphuric acid rarely contain beyond 4 per cent. of copper.

The *principal sources of pyrites* will now be mentioned without separating the cupreous from the non-cupreous, because no strict limit can be drawn. Some kinds of pyrites contain so little copper (below 1 per cent.) that it cannot be utilized; and these go with the totally non-cupreous ores.

The most important *German* pyrites bed is that of *Meggen* in the Siegen district, in Westphalia, 3 miles from the Altenhunden station on the Ruhr-Sieg railway. This bed occurs along with heavy spar in the so-called "Kramenzel;" it is known for a length of 2000 fathoms; and its thickness changes from $\frac{5}{4}$ to 3 fathoms (Wagner's 'Jahresbericht,' 1865, p. 221). The same authority states it to be "grey iron-pyrites," quite uncrystalline, free from arsenic [?], of equal composition throughout, and containing 47·50 sulphur, 43·55 iron, 0·32 carbon, 8·22 silica; but this analysis is far too favorable if referred to the bulk of the ore. The mass of ore above the bottom of the valley is estimated at 4¼ million tons; how far the ore may go down below the bottom of the valley is as yet unknown. The quantity got yearly has been stated in the table at p. 85.

This ore has not an attractive outward appearance; its colour is slate-grey; but it burns very well in the kilns, and it would be even more valuable if the zinc contained in it did not prevent its burning completely. Fresenius analyzed a large average of this Meggen ore from the "Sicilia" pit, and found 45·42 per cent. of sulphur and only 0·02 per cent. of arsenic; this agrees with Pattinson's analysis of the average sample of a whole cargo (in his paper read to the British Association at Newcastle-on-Tyne in 1864) which shows:—

	per cent.
Sulphur	45·60
Iron	38·52
Lead	0·64
Thallium	trace
Zinc	6·00
Cobalt	trace
Arsenic	trace
Lime	0·11
Insoluble, silica &c.	8·70
Oxygen (as Fe_2O_3)	0·37
Moisture	0·36
	100·30

According to H. A. Smith, Westphalian pyrites contains 1·878 per cent. of arsenious acid; but it is strange that such a high percentage of arsenic should have escaped other observers. Hjelt (Dingl. Journ. ccxxvi. p. 175) indeed only found 0·30 per cent. As. Latterly the pyrites obtained is rather poorer, and its average percentage of sulphur only amounts to 41 or 42 per cent. Owing to the competition of cupreous pyrites, its exportation to other countries has very much decreased of late; but in Germany its consumption has very much increased.

There are smaller beds of pyrites in several other places in Germany, such as those near Goslar, near Schwelm in Westphalia, near Merzdorf in Silesia, &c. Their production is only small compared with that of the Meggen pyrites. The pyrites of the Rammelsberg in the Harz, according to Mène, contains 48·4 per cent. of sulphur (probably only picked lumps). The cupreous pyrites of the same place is stated by Hilgenfeld to contain:—

Copper	12·22
Lead	2·43
Iron	39·10
Zinc, Manganese, Cobalt, Nickel	1·23
Arsenic	0·18
Antimony	0·16
Sulphur	44·65
Selenium, Thallium, Indium, Bismuth	traces
	99·97

The bed of *Schwelm* in Westphalia, in the Devonian formation, has a thickness of from 10 to 33 feet, over a surface of nearly 150 acres, and is covered by rich iron-ore; the pyrites itself consists to the extent of two thirds of powder mixed with well-crystallized pieces. The ore contains about 40 per cent. of sulphur, and more or less clay, which is removed by washing; after this it is sold to the vitriol-makers, who like it on account of its freedom from arsenic (Dingl. Journ. ccxxviii. p. 283); Hjelt, however, found more arsenic in it than in Meggen pyrites.

On the Island of Wollin a pyrites bed is found in a bed of marl belonging to the chalk formation.

In *Hungary* very good pyrites occurs at Schwellnitz, containing 46 or 47 per cent. of sulphur and a few per cent. of copper. It is heavy, but very porous, and burns very well; but it is rather explosive. This ore is used at the Aussig works.

In *Styria* (Riedl, Zeitschr. f. d. chem. Grossgewerbe, ii. p. 567), in the Saun valley, a number of beds of very pure but easily decomposable pyrites occur in the clay porphyry, with a percentage of 48 to 52 of sulphur. It is used in the chemical works at Hrastnigg and in Bohemia.

In *Switzerland*, in the Canton of Wallis, a pyrites occurs which does not seem to have found any technical application as yet. Its composition, according to an analysis made in the author's laboratory, is :—

Sulphur	50·46	(of this 0·05 as lead sulphate in the insoluble residue).
Iron	44·55	
Lead	0·37	
Lime	1·13	
Magnesia	0·11	
Carbonic acid	1·01	
Silica, Iron peroxide, Alumina	1·70	(insoluble)
Moisture	0·40	
	99·73	

Of the *French* sulphur-ores the most important are those of Chessy (cupreous) and of Sain-Bel (non-cupreous) near Lyons; a smaller bed exists at Alais in the south of France. Mène has examined a large number of French (and other) pyrites, and has tabulated his results as follows ('Moniteur Scientifique,' 1867, p. 410) :—

Mène's Analyses of Pyrites.

I. Yellow Pyrites (see p. 88) (all arsenical).

	From Chessy and Sain-Bel.				Aiguebelle (Savoy).			Ainbarbar (Algeria).		Allevard (Isère).	Gard.		Car-cassonne.	Allier.
Density	4·6106	4·6322	4·6191	4·6201	4·6406	4·7323	4·6892	4·5891	4·4930	4·7500	4·7468	4·7152	4·7428	4·8033
Silicic acid......	9·8	11·0	9·6	9·5	11·2	8·2	9·2	13·5	12·0	6·5	7·0	10·5	6·0	2·5
Alumina	3·5	4·1	3·6	4·0	4·1	3·0	3·6	4·2	3·8	2·0	1·1	2·2	1·0	0·0
Loss	0·2	0·4	0·3	0·0	0·2	0·5	0·4	0·5	0·6	0·5	0·0	0·6	0·2	0·4
Water	0·2	0·3	0·1	0·1	1·5	0·4	0·3	0·2	0·0	0·4	0·1	0·3	0·2	0·2
Sulphur	46·6	45·2	47·6	46·7	44·5	47·4	47·0	44·4	45·6	48·5	49·7	47·4	49·1	44·2
Iron	39·7	39·0	38·8	39·7	38·5	40·5	39·5	37·2	38·0	42·1	42·0	39·0	43·5	52·7
Limestone	......	......	......	......	......	......	......	......	......	......	0·1	......	......	......

II. Grey Pyrites.

Ditto from Coal-pits.

	From Champagne.				St. Etienne.	Creuzot.	Mons.
Density	4·1872	4·1709	4·1695	4·1741	4·1797	4·1822	4·1756
Sulphur...............	47·3	45·0	46·8	42·7	49·2	49·0	45·0
Iron	41·5	39·7	41·6	47·0	42·1	43·0	38·7
Water	2·0	2·5	1·8	1·9	6·3	5·5	1·8
Silica...................	7·2	10·0	8·0	6·5	0·9	0·8	12·0
Alumina	1·5	2·1	1·6	1·4	0·3	0·5	2·5
Loss	0·5	0·7	0·2	0·5	1·2	1·2	0·9

III. Foreign Pyrites.

	From Rammelsberg.	Rocheux (Belgium).	Drontheim.		South Australia.
Density	4·6855	4·2773	4·6652		4·7081
Sulphur........................	48·4	48·1	49·7	50·0	48·7
Iron	42·1	42·2	42·8	43·3	42·0
Gangue	6·0	8·5	4·0	4·7	4·2
Copper	1·9	0·2	—		2·8
Zinc	1·2	0·7	—		1·2

According to Girard and Morin (Compt. Rend. July 26, 1875), the pyrites from the Rhone and Sain-Bel, on an average, contains 46 to 48 per cent. of sulphur and 10 to 12 per cent. of gangue, consisting of clay, sand, and barytes. In the southern part of the district of Sain-Bel the percentage of sulphur rises to 50 or 53, and the gangue is inconsiderable and free from barytes; arsenic is not present in quantities sufficient for determination. In the district of St. Julien (Le Gard) pyrites is not found in the clay-slate, as at Sain-Bel, but in the Lias or Trias; the sulphur varies from 40 to 45 per cent.; the gangue is calcareous, and varies from 3 to 6 per cent.; arsenic is present up to 0·1 per cent., sometimes also fluor spar in quantities sufficient for estimation. The pyrites from Ardèche contains from 45 to 50 per cent. of sulphur; the gangue is clay, free from lime; arsenic occurs up to 0·3 per cent.; fluor spar sometimes occurs in injurious quantities: the hydrofluoric acid given off from it in one case destroyed the glass apparatus for spreading the nitric acid; and the latter thus got to the chamber-bottom and corroded the same.

In 1874 there were used in France 178,400 tons, of the value of £240,000. Of this the beds of Sain-Bel, which supply two thirds of the French factories, supplied 120,000 tons, those of St. Julien (in the department Gard) 24,600 tons, those of Le Soulier (Gard) 6000 tons, those of Soyons (Ardèche) 900 tons. From Belgium, Norway, and Spain 18,000 tons were introduced. Girard and Morin also give twenty-three analyses of French and five of foreign pyrites used in France.

According to Scheurer-Kestner (Wurtz, Dict. de Chimie, ii. p. 138) the pyrites from Chessy and Sain-Bel contains 45 to 48 per cent. of sulphur with very little arsenic and selenium, that from Chessy also 1 or 2 per cent. of copper and zinc; the copper is obtained from the cinders, at least at the Chessy works themselves, by allowing them to lie for a time and moistening them: the liquid running off contains copper and zinc sulphates; and the copper is got from it by cementation. Nearly all French works, as well as those in Alsace and Switzerland, get their ore from those two pits; only those of the Gard and of Marseilles get it from Alais, where the pyrites contains 38 to 42 per cent. of sulphur; a few factories in the north of France use Belgian pyrites.

In *Belgium* (for its production of pyrites see p. 85) there is a rich pyrites, the great friability and softness of which do not tell in its favour. Its production has remained stationary. The following are analyses of this pyrites :—

	a.	*b.*	*c.*	*d.*	*e.*	*f.*
Sulphur	42·80	35·50	46·20	45·01	50·00	45·60
Iron	36·70	38·60	40·50	39·68	43·61	38·52
Ferric oxide	7·23	4·24	2·20			
Oxygen in ferric oxide	......	......	......	0·32	0·18	6·00
Lead	0·92	0·65	0·41	0·37		
Zinc	0·40	5·26	0·22	1·80	1·75	
Arsenic	0·20	0·31	0·41	trace	trace	trace
Thallium...........	......	......	......	trace		
Alumina	trace					
Silica	8·86	14·90	9·10	12·23	2·85	9·00
Carbonic acid	......	......	......	......	0·73	
Calcium carbonate	0·84	trace	......	......	......	0·11
Lime	......	......	......	0·25	0·92	
Water	1·46	0·56	0·42	0·25	0·10	0·36
	99·41	100·02	99·46	99·91	100·14	99·59

(*a*, *b*, and *c* by Clapham in Richardson and Watts's 'Chemical Technology,' vol. i. part iii. p. 14; *d*, pyrites from Rodieux near Spa, *e* from Santon's pit on the Meuse, both by Pattinson, *l. c.*; *f* by MacCulloch, Chem. News, xxvii. p. 125.)

The Belgian pyrites is usually only got as a by-product in the getting of lead- and zinc-ores in the provinces of Liège and Namur; it is either microcrystalline or crystalline or in bulbous pieces with a concentrically fibrous structure. Its quality is uneven. It is mostly used locally and in the north of France; the export to England seems to have ceased. According to H. A. Smith it contains, on an average, 0·943 per cent. As_2O_3.

Italy possesses pyrites in several places. That from the Val d'Aosta contains 48 to 50 per cent. of sulphur, but also much arsenic, and is very friable. It is used at the factory of Sclopis, Bechis, and Co., at Turin. The pyrites of Pallanza only contains 30 to 35 per cent. sulphur, also ½ to 1 per cent. of nickel.

Analyses by......	Pattinson. (From Genoa).	Clapham. (Tuscany.)	Browell and Marreco.	H. A. Smith.
Sulphur	47·00	48·4	44·60	
Iron	42·20	44·5	40·26	
Lead	trace			
Zinc	trace			
Lime	0·21			
Magnesia	0·60			
Arsenic	trace	......	......	0·943 As_2O_3.
Insoluble (silica)	9·20	3·6	14·30	
Oxygen as Fe_2O_3	0·24			
Water	0·17			
	99·62			

The pyrites imported to England *viâ* Genoa consisted of a conglomeration of smaller and larger crystals, and consequently was of a very friable nature; its falling to pieces in the burners deterred the manufacturers from using it more extensively.

Great Britain possesses several deposits of pyrites, but none of very great importance. In Cornwall and Devonshire pyrites of the following composition is found:—

	Pattinson.	Clapham (8 analyses).
Sulphur	27·00	24·013–34·880
Iron	22·69	27·076–60·676
Copper	2·00	0·400– 4·600
Lead	trace	0· – 7·446
Zinc	1·23	0· – 9·086
Lime	0·22	Gypsum 0· – 0·596
Carbonate of Lime	......	0· – 3·579
Magnesia	0·12	
Arsenic	0·32	0· – 1·160
Insoluble (silica)	45·60	2·000–38·676
Oxygen as Fe_2O_3	0·13	
Moisture	0·64	
	99·95	

Cleveland pyrites (from the north of Yorkshire) is only used in a local factory; in 1874, 500 tons of it were obtained. Composition (according to Pattinson's analysis):—

Iron bisulphide (corresponding to 27·18 sulphur).	52·12
Iron protoxide	11·92
Alumina	8·10
Lime	0·27
Magnesia	1·00
Carbonic acid	2·40
Insoluble in acid	11·12
Water	12·86
	99·79

In *Ireland* there are large beds of pyrites, especially in the county of Wicklow; and up to about 1862 this Irish ore supplied a very large portion of the pyrites used in England. In 1860 still 40,000 tons of it were imported into the Tyne river; but in 1863 the importation had fallen to 4000 tons, and has long since ceased entirely. The same has been the case in Lancashire; and only a few works in Ireland itself burn this kind of pyrites. It is found in the county of Wicklow in beds from 6 to 50 feet in thickness, which overly siliceous clay-slate. The beds go down to depths of 80 to 100 fathoms. The bulk of the ore contains only 30 to 35 per cent. of sulphur. A small quantity only of richer ore (analyses *a*, *b*, *c*) has been found in the valley of Ovoca. The Irish ore is too hard and slaty, and does not burn well; it requires a great heat, and consequently deep kilns. It nearly always contains copper, but rarely sufficient to pay for extracting it, from which standpoint the following analyses must be judged. Its production (formerly much more considerable) had in 1874 fallen to 18,272 tons.

	Pattinson.	Clapham.			
	a.	*b.*	*c.*	*d.*	*e.*
Sulphur	44·20	40·410	42·128	37·975	34·676
Iron	40·52	32·222	35·000	34·650	42·400
Copper	0·90	4·133	2·400	2·400	1·333
Lead	1·50	2·963	1·600	1·080	1·593
Zinc	3·51	...	...	...	...
Arsenic	0·33	...	0·602	0·400	0·183
Lime	0·24	...	...	...	...
Insoluble	8·80	17·676	18·676	22·500	20·000
Moisture	0·09	...	...	...	...
Oxygen as Fe_2O_3	0·25	...	...	...	...
	100·34	97·404	100·406	99·005	100·185

In *England* also here and there pyrites picked from coals, "coal-brasses," are used, especially for lighting the burners, or for getting up their heat if it has got too low. If *quite free from adhering coal*, they are very pure (according to R. D. Thomson, in Richardson & Watts, *l. c.* p. 15, 53·55 sulphur, 45·07 iron, 0·70 manganese, 0·80 silica); but they are not actually employed in this state; and on the whole they cannot be recommended very much, on account of the formation of carbonic acid. In 1874 10,000 tons of this material was got, but probably mostly worked up for copperas and Venetian red.

Swedish pyrites, from Fahlun, varies between 43 and 48 per cent. of sulphur. It has only been imported into England in small quantities. This ore is obtained as a by-product in the getting of copper-ores, and is said to exist in enormous quantity; but, owing to the difficulty of transit, its exportation does not pay. It is said to burn well.

	Pattinson.	Browell and Marreco.
Sulphur	43·70	38·05
Iron	39·01	42·80
Copper	0·60	1·50
Lead	0·12	
Zinc	2·57	
Lime	0·85	
Magnesia	0·69	
Arsenic	trace.	
Insoluble	11·66	12·16
Oxygen, as Fe_2O_3	0·22	Oxygen and loss 5·49
Water	0·20	
	99·62	100·00

In *Norway* there exist very large beds of pyrites, both free from and containing copper. Of the many pits formerly worked there, all those had to stop which produce ores with from 35 to 40 per cent. of sulphur. But of the richer ores, even of those free from copper, a few have maintained their position permanently, because they burn well, are easily lighted, keep the heat well, do not "scar," &c. They are mostly hard and difficult to break. The most considerable pits are those of Ytteröen, which export *viâ* Drontheim; they supply 6000 to 8000 tons per annum. Other pits exist thirty miles from Drontheim, on the Hardanger Fjord, near Bergen, &c. The Norwegian pyrites is mostly more in favour as a sulphur-ore (excepting its difficult breakage) than as a copper-ore; its cinders do not very well suit the copper-works. H. A. Smith states the arsenic in hard Norwegian pyrites to be on an average =1·649 per cent., in softer ores =1·708. This is contradicted by all other analyses, as well as by the distinct assertion of Hjelt (*l. c.*), who found mere traces of arsenic in hard Norwegian pyrites. This statement of Smith's, like all his others, must be received with great caution.

	Pattinson.		MacCulloch.	
	Ytteröen ore.	Drontheim ore.	I.	II.
Sulphur	44·50	50·60	46·15	38·17
Iron	39·22	44·62	44·20	32·80
Copper	1·80	trace	1·20	1·10
Zinc	1·18	1·34	2·10	2·32
Lead	...	trace	...	...
Lime	2·10	trace	...	...
Calcium carbonate	...	...	2·55	11·90
Magnesia	0·01	trace	...	...
Magnesium carbonate	...	...	...	1·08
Carbonic acid	1·65	...	...	...
Arsenic	...	...	...	trace.
Insoluble	9·08	3·15	3·20	12·20
Oxygen, as F_2O_3	0·45	...	...	...
Moisture	0·17	0·20	0·40	0·25
	100·16	99·91	99·80	99·82

Spain and Portugal possess the largest known beds of pyrites. It is cupreous, and distinguished by its very good behaviour in burning; so that the burners have been built very much lower for it, and much labour is saved. This pyrites has only been worked again since 1855; but the Romans, and before them the Phœnicians and Carthaginians, knew it very well, as is shown by many traces. The bed, however, was at that time only worked where it was richest in copper. According to Schönichen (Dingl. Journ. clxx. p. 448) all the beds are within a belt of five leagues width, reaching, parallel to the Sierra Morena, from the western frontier of the province of Seville, across the hilly country situated to the south of this, right through Portugal to the Atlantic Ocean —a length of 30 leagues. The prevailing rocks in that country are clay-slate and crystalline slates; but parallel to the granitic tract of the Sierra Morena felsite-porphyry and quartzite have broken through the slate, and only in the neighbourhood of such dykes are the pyrites beds found. Their shape is that of large lenticular pockets in the metamorphic clay-slate, from 20 to 36 fathoms thick, and extending to a length of 170 to 260 fathoms. The whole bed is filled with pure pyrites, without any visible gangue. This is in a few places found already at 1 or 2 fathoms below the surface, undecomposed, and in a sandy state; so that it can be got by daylight work. In other places the zone of decomposition reaches from 10 to 50 fathoms downwards. The percentage of copper varies from 2½ to 40; but ores with more than 10 per cent. of copper are only contained in small vertical zones within the large masses. Only these "black" ores were the object of the mining operations on the part of the Phœnicians and Romans. The quantity of pyrites existing there is almost inexhaustible, and can certainly supply the requirements of mankind, both of copper and of sulphur, for thousands of years to come.

Special highways, and latterly also railways, have been made, in order to facilitate the communication with the ports of Huelva, San Lucar de Guadiana, and Pomaron; but a great deal of the ore is still conveyed for some distance on mule-back.

Of the many companies which had been formed for working this ore most have ceased to exist; and only four or five of them have remained, all of them in English hands. The smallest of these is the Buitron Pyrites Company, which works the mines of Buitron and Poderosa. The Tharsis Sulphur and Copper Company possesses much more extensive mines, a railway of its own, a wharf at Huelva, and also a number of works in England and Scotland for the wet extraction of the copper from the cinders returned to them. The Tharsis ore is very good, but very soft, and makes much dust in breaking. The San-Domingo mine lies in Portuguese territory; its ore is known as Mason's ore, and is considered superior to all others, so that it commands a better price. The last, but largest, of these companies is the Rio-Tinto Company, which has thrown such large masses of pyrites into the English market that, from 1875 to 1876, prices receded by more than one third. Its ore is also of excellent quality. The mines of Carpio and Lagunazo, in the province of Huelva, are not yet worked for exportation.

The Spanish (and Portuguese) pyrites contains never less than 46, and up to 50 per cent. of sulphur, besides 3 to 4½ per cent.

of copper, which, however, by most of the English buyers, is not bought, but returned in kind to the seller in the shape of cinders from the pyrites-burners. The value of the copper (if bought) is still fixed by the so-called "Cornish assay"—that is, a process of dry assaying only known to a few assayers living at Redruth and other places in Cornwall, the great inaccuracy of which is perfectly well known to all parties concerned; it shows, for instance, only 2 per cent. if 4 per cent. is actually present; and from this difference the buyer must pay the cost of extracting the copper and his own profit, since the price to be paid for the copper *in the ore* by Cornish assay is sometimes higher than the value of a similar quantity of copper *metal*. This remarkably irrational system has not hitherto been done away with for sales.

In Germany also a few years ago a number of manufacturers united in working Spanish pyrites (especially Rio-Tinto ore), and in delivering all their cinders to the Duisburg copper-works. The Oker works also use similar ores, which they work up themselves for copper.

The ore of the three principal companies is very similar in composition; its analysis is as follows:—

	Pattinson.				Claudet (San-Domingo ore).	MacCulloch (San-Domingo ore).
Sulphur	48·00	49·60	44·60	49·30	49·00	49·80
Iron	40·74	42·88	38·70	41·41	43·55	42·88
Copper	3·42	2·26	3·80	5·81	3·20	2·26
Lead	0·82	0·52	0·58	0·66	0·93	......
Zinc	trace	0·10	0·30	trace	0·35	0·10
Lime	0·21	0·18	0·14	0·14	0·10	0·18
Magnesia	0·08	trace	trace	trace	......	......
Thallium	trace	trace	trace	trace	......	......
Arsenic	0·21	0·28	0·26	0·31	0·47	0·28
Insoluble	5·67	2·94	11·10	2·00	0·63	2·94
Oxygen (as Fe_2O_3)	0·09	0·15	0·23	0·25	1·07	......
Moisture	0·91	0·95	0·17	0·05	0·70	0·95
	100·15	99·86	99·88	99·93	100·00	99·39

Some descriptions of Spanish pyrites are in bad odour with the manufacturers as "explosive" or "detonating," because they decrepitate in the kilns shortly after lighting with loud detonations, and thereby make so much fine powder that the burners are stopped up and "scars" are formed. The reason of this detonating property is probably to be sought in the presence of hydrated silicates (zeolites) in the ore.

The percentage of arsenic, according to H. A. Smith, in Tharsis ore amounts to 1·651, in San-Domingo ore to 1·745 per cent. As_2O_3 on an average. According to Hjelt the average percentage of As in Spanish ores is 0·91.

Proportional value of poor and rich Pyrites.

It is no matter of surprise that the rich and at the same time well-burning Spanish ores, and the descriptions similar to them everywhere, where they could be imported, have driven the poor ores out of the field. An ore of 35 per cent., like that from Wicklow, even for the same weight of sulphur, has much less value than a 45-per-cent. ore. The wages for breaking and burning the ore in both cases must be ruled by the gross weight of the ore, and consequently for equal weights of sulphur come to much more with poor than with rich pyrites; moreover, under conditions otherwise equal, the unburnt sulphur in the cinders is the same by weight. If, for instance, 5 per cent. of sulphur are left in the cinders, this amounts with 35-per-cent. ore to $\frac{5}{35}=\frac{1}{7}$; with 45-per-cent. ore to only $\frac{5}{45}=\frac{1}{9}$; the proportion to be kept in view is accordingly not $35:45=7:9$, but $30:40=3:4$. Furthermore, the same holds good of cost of plant and repairs, and of wages, and, lastly, since the poor ores generally contain no copper, also of the cost of removing the cinders.

Therefore, unless the burning is nothing but a preparation for the metallurgical treatment, where the sulphur is quite a secondary matter, the ores poor in sulphur are always avoided as much as possible.

Analyses of Pyrites.

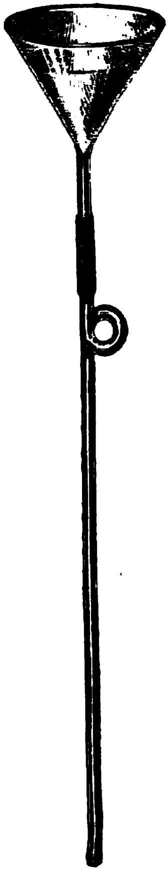
In the analyses of pyrites for technical purposes, in the first instance their percentage of sulphur is taken into account; and it is therefore mostly the custom to estimate only this and, perhaps, also the moisture. If the ore has afterwards to yield copper, this must of course also be regarded; but where the copper, as is mostly the case, is not bought by the vitriol-maker, but the cinders are returned to the seller, the estimation of copper is generally omitted in the chemical works as unnecessary. This restriction to the estimation of sulphur ought, however, only to take place with pyrites from well-known localities, whose general composition and properties are well known, and where the salient point is only the percentage of the most important constituent, viz. the sulphur. In Germany, where the pyrites is not paid for by percentage of sulphur, an estimation of the same is still desirable in the interest of the manufacturer; in England this is absolutely necessary. Each cargo, even each portion of a cargo going to a separate buyer, is sampled in the presence of both the buyer's and seller's agents, according to well-understood rules; the sample is broken up, reduced, and sealed up in bottles, which are sent to an analytical chemist (generally mentioned in the contract note); this chemist's certificate rules the price to be paid for the pyrites down to ¼ per cent. If, for instance, a sale has been made at 6*d.* per "unit," this means that for each per cent. of sulphur found the sum of 6*d.* per ton is paid; thus for 48¼ per cent. of sulphur 48¼ × 6*d.* = 24*s.* 1½*d.* per ton. The ton is generally calculated = 21 cwt.; that is to say, the buyer receives an allowance in weight of 5 per cent.

The first treatment of the pyrites in analyses, in the majority of cases, is by the *wet* way, by fuming nitric acid or aqua regia; but the prescriptions differ in details. The solution has frequently been made, from Fresenius's prescription, by means of red fuming nitric acid, which it is sometimes difficult to obtain free from sulphuric acid, and which is unpleasant to handle. In lieu of this sometimes chlorate of potash along with hydrochloric acid, or, still better, with nitric acid of 1·36 sp. gr., have been used. The author has always found the best, safest, and cheapest way to be that by aqua regia, made from 1 part of fuming hydrochloric acid and 3 or 4 parts of nitric acid of 1·36 to 1·4 sp. gr. The mineral is converted into an impalpable powder and passed through the finest silk gauze; the triturating ought to be done first in a steel mortar or by wrapping it up in paper and smashing with a hammer, and then in an agate mortar, *not* in a porcelain or Wedgewood mortar. The powder is treated with about 50 parts of aqua regia; if no reaction takes place at once, it should be gently heated on a water-bath till the reaction sets in; but then the beaker should be removed instantly from the water-bath, and only replaced when the reaction slackens; thus the solution is generally complete in 10 minutes. The operation, of course, has to be done in a large beaker, or, still better, in an Erlenmayer's flask covered by a funnel or a watchglass, lest any loss should take place by spurting; and the work must be done in a draught-place, on account of the mass of acid vapours given off. If the solution should not be perfect after heating some time, some more aqua regia has to be added and the heating continued; but mostly this will be caused by the powder not being sufficiently fine, and the analysis in this case cannot easily be finished. In this way of resolving the ore, which is both quick and safe, the disagreeable separation of sulphur happens extremely rarely.

The residue from the solution will contain silica and silicates, perhaps a little lead or barium, both as sulphates. Although their sulphur is thus not estimated, no harm is done, as it is anyhow valueless to the manufacturer. Lead sulphate is pretty soluble in concentrated acids, but it is almost entirely precipitated again by the immediately following treatment.

At all events the whole of the nitric acid present must be destroyed or removed, because the estimation of sulphuric acid by barium chloride in the presence of nitric acid or its salts gives results much in excess of the truth. The whole is therefore evaporated to dryness on the water-bath with an excess of hydrochloric acid, by which at the same time all silicic acid dissolved is made insoluble. The mass is again moistened with strong hydrochloric acid; and if on gently heating no yellow vapour and no smell of nitrous products are perceived, it is diluted with hot water and the solution filtered from the residue. Care must be taken not to employ too much hydrochloric acid, as barium sulphate is not quite insoluble in hot concentrated acids; on the other hand, enough acid must be present to dissolve all salts of iron, which cannot be doubtful if the colour and behaviour of the residue are observed. The clear solution is brought to *full boiling*; and to it during boiling a *hot* solution of barium chloride is added. Lest too great an excess of this be used, it is preferable to use a measured quantity of a concentrated solution of known strength, but more than sufficient for precipitating all the sulphuric acid present. If the process is carried out as described here, the barium sulphate settles down completely in a few seconds, leaving a perfectly clear liquid, and nothing of the precipitate passes through the filter. It is quite unnecessary to allow more time for the settling. If the operation is carried on as described, the filtrate never becomes cloudy afterwards; on the other hand, the work is extremely hastened by filtering the liquid in the boiling-hot state a few minutes after precipitation. A Bunsen's filter-pump acts rather too strongly in this case; but it is very useful to employ a simple contrivance indicated many years ago by Piccard, which does excellent service in innumerable other analytical operations, viz. a glass tube attached to the funnel by means of an elastic joint, with a loop, causing a continuous jet of liquid to issue at the bottom (fig. 8). The straight part below the loop may be 8 or 10 inches long; the filter must be pressed tight to the sides of the funnel to prevent any air being sucked in. When this contrivance is used, which does not act so violently as a Bunsen pump, the liquid, so long as there is not too much precipitate on the filter, runs through in a continuous jet.

Fig. 8.



At first only the clear liquid is poured off as completely as possible from the dense granular precipitate; this is covered with *boiling* water, acidulated with a few drops of hydrochloric acid; the liquid is boiled for a few moments, and can be decanted again in about two minutes' time. This is repeated another twice or three times, but without adding any more hydrochloric acid; the precipitate is washed onto the filter; and after very little washing the filtrate will be found perfectly neutral and free from dissolved matters. The filter is dried, the precipitate taken out, and the filter burnt, preferably in a platinum crucible laid on its side; then the precipitate is put in and ignited, not too strongly; and for each 100 parts of barium sulphate found 13·734 parts of sulphur are calculated. The ignited barium sulphate ought not to cake together; on moistening, it ought not to give an alkaline reaction; and on heating with dilute hydrochloric acid and filtering, no barium salt ought to be found in the solution.

Sometimes it happens, even if the solution before precipitation was rather strongly acid, that the precipitate is stained yellowish by precipitated ferric oxide or basic ferric sulphate, which cannot be removed even by boiling with dilute hydrochloric acid. Very rarely the quantity of this ultimately remaining in the barium sulphate will amount to more than a small fraction of 1 per cent., and it can accordingly be neglected for technical purposes. But if absolutely exact work is required, the barium sulphate after ignition must be digested with moderately strong hydrochloric acid, washed, dried, and ignited again; or, in the worst case, it must be fused with sodium carbonate, the fused mass extracted with hot water, acidulated, and precipitated a second time.

When the precipitation with barium chloride has been made in this way, which requires no more trouble than working in a rougher way, the results are altogether accurate, for which the authority of Fresenius vouches as to the principal points. Certainly the process as usually carried out (also by Fresenius's prescription) takes a good deal of time; and this probably explains most of the attempts at replacing the gravimetric method in this case by a volumetric one. But if the work is done as described, if quite boiling solutions are used, even the barium-chloride solution employed hot, if the clear liquid is decanted at once, the precipitate boiled again with water, decanted again, &c., the whole work, even with large quantities of precipitate (2 to 3 grams), takes little more, and with small quantities (for instance, when estimating the sulphates in soda-ash) often less time than the volumetric analysis, and at the same time affords the advantage of greater accuracy.

To be sure the assertion has been made, by a firm of commercial analysts, Messrs. Teschemacher and Smith, of London, that sulphuric acid under no circumstances can be exactly estimated gravimetrically by barium chloride (Chem. News, xxiv. pp. 61, 66); and they accordingly prefer a volumetric method, proposed a long time before them by Wildenstein (Zeitschr. f. analyt. Chemie, i. p. 432). They use a standard solution of barium chloride, which is added to the boiling-hot solution of pyrites until a filtered sample gives no more precipitate with barium chloride. In order to be able to use it *hot*, they do not add the barium-chloride solution, but *weigh* it out of a dropping-vessel. The other precautions upon which they insist, such as complete oxidation of the sulphur, driving off of the nitric acid, avoiding a large excess of hydrochloric acid, contain nothing new. They certainly assume a much larger solubility of barium sulphate in dilute hydrochloric acid than any other observer. Glendinning and Edger (ib. p. 140) explain the fact mentioned by Teschemacher and Smith, that the clear filtrate from the barium sulphate frequently becomes cloudy after some time, by the circumstance that with the barium sulphate ferric sulphate is easily carried down, which is only dissolved again in washing, and which, of course, gives a precipitate with the barium sulphate in excess; this, however, must affect the accuracy of Teschemacher and Smith's method precisely as much as that of the ordinary one. This certainly cannot be disputed; and it is advisable to keep the filtrates from the barium sulphate for 24 hours in order to see if they remain clear; the author has done this scores of times, but never got any afterprecipitate when the process had otherwise been properly carried out.

In any case the process of Teschemacher and Smith, as prescribed by them in detail, is not a short one. A little more convenient, but not very accurate, certainly not sufficiently so for buying and selling, is the modification first proposed by Wildenstein (Fresenius, 'Quant. Anal.' 6th (German) edition, i. p. 396). The process has reached the utmost simplicity as employed in some factories for estimating the sulphates in black ash &c. The liquid is brought to the boil in a porcelain dish, barium-chloride solution is added from a burette; from time to time a few drops are taken out with a glass tube, filtered through a miniature filter onto a glass plate resting on a black background, upon which a number of drops both of dilute sulphuric acid and of barium chloride have been put. If the filtrate still gives a cloudiness with a barium-chloride drop, easily visible on the black ground, the little filter is thrown back into the dish, more barium-chloride solution is added from the burette, another test is made, and so forth. The end is attained when a filtered drop gives an extremely small cloudiness both with a drop of barium chloride and with one of sulphuric acid. This process yields results pretty near the truth; with very small quantities, however, the filtering, washing, and igniting can be done almost as quickly as the titrating; the drying on the sand-bath need not be reckoned, as it involves no labour.

The same objection, viz. that they do not in the end save so very much time, and that after all they are not so accurate, can be made to the various other volumetrical methods of Carl Mohr, Clemm, Wildenstein (2nd method), Schwarz, Pappenheim, and others which are described in the treatises of Fresenius and Mohr; they do not offer any advantage worth speaking of in competition with the direct titration with barium chloride. This latter method is certainly employed regularly by some chemists in lieu of the estimation by weight.

The estimation of sulphur in pyrites has also been tried in other ways, principally with the object of saving time, with a degree of accuracy believed by the authors to be sufficient.

Best known probably is the method of Pelouze (Compt. Rend. liii. p. 685; Ann. de Chim. et de Phys. [3], pp. 63, 415). The finely powdered pyrites is mixed with chlorate of potash, common salt, and an exactly weighed quantity of sodium carbonate, and ignited, which can be done in an iron spoon. The fluxed mass is dissolved in water, filtered, the residue washed, and the soda not converted into sulphate estimated alkalimetrically. This process continued to be recommended in French treatises till very recently, although its inaccuracy was established and the sources of error partly demonstrated by many chemists, such as Barreswil, Bottomley, Bocheroff, the author, and especially Kolb ('Notes sur l'Essai des Pyrites de Fer'). Kolb found the sources of error on the one hand in the formation of sodium silicate, on the other hand in the decomposition of potassium chlorate in the presence of ferric oxide into chlorine, oxygen, and caustic potash. Kolb himself proposes to flux the finely powdered ore with 5 grams sodium carbonate and 50 grams copper oxide at a dark-red heat, to heat the fluxed mass with hot water, to filter, and to estimate the remaining soda volumetrically in the filtrate. This process at any rate requires further trial and confirmation.

In the Freiberg works 1 gram of finely ground pyrites is mixed with 2 grams sodium carbonate and 2 grams saltpetre; the mixture is fluxed in a small iron dish in a red-hot muffle-furnace, dissolved in hot water and filtered into a beaker in which there is hydrochloric acid for saturating the soda in excess. Then the filtrate is brought to boiling and the sulphuric acid estimated by standard chloride-of-barium solution. This is accordingly only a resolving of the ore in the dry way, long known, as against that in the wet way; and it certainly saves very little time, if any. With careful work both ways give identical results (Holland, 'Chem. News,' xxvii. p. 15).

Hayes ('American Chemist,' v. p. 271) describes a method of resolving pyrites with alcoholic soda and lime, the advantages of which are in no way evident.

Fresenius has also recommended latterly (Zeitschr. f. anal. Chemie, xvi. p. 335) to resolve pyrites by fluxing it with 20 parts of a mixture of 2 parts of dry sodium carbonate entirely free from sulphate, and 1 part of pure potassium nitrate, conducting carbonic acid into the solution for the precipitation of lead, boiling the residue with a solution of sodium carbonate and then with water, acidulating with hydrochloric acid, and repeatedly evaporating for the expulsion of nitric acid, after which the process is carried on as usual, the precipitation taking place by barium chloride. This process is much more troublesome and tedious than that described above by dissolving in aqua regia, and it cannot well be applied to larger quantities than ½ gram pyrites; its advantages are therefore doubtful, at any rate for technical purposes.

Fahlberg and Iles (Ber. d. deutsch. chem. Ges. xi. p. 1187) recommend fluxing the sulphur-ore with caustic potash (25 grams to 0·1 gram of S) in a silver crucible for 15 to 20 minutes, lixiviating the mass, oxidizing the lower oxides of sulphur by bromine-water, and precipitating by barium chloride.

The so-called *mechanical pyrites assay* of Anthon (Dingl. Journ. clxi. p. 115) is too rough and unreliable even for very simple purposes. The prescription is to observe the space taken in a glass tube by 8 grams pure pyrites in fine powder well shaken down, on the one hand, and by 8 grams of fine quartz powder on the other, then to divide the portion of the tube between the two levels into 50 parts. Thus an ore to be estimated is said to be valued down to 2 per cent., if 8 grams of it are put into the tube.

It has been said above that it is sufficient to estimate the sulphur in a pyrites whose nature is otherwise known. If, however, the pyrites is of unknown composition, its value for acid-making can only be estimated by a complete determination of all its constituents according to the rules of mineral-analysis. If it contains, for instance, *calcium carbonate*, this on burning will retain its equivalent of sulphuric acid; if *calcium sulphate* is present from the first, its sulphuric acid has to be deducted from the whole quantity of sulphur found. If *lead* has been found, an equivalent of sulphur must be considered as practically lost; and the same is the case with *zinc*,—because the sulphates of both metals are hardly or not at all decomposed at the temperature of a pyrites-burner. Frequently *arsenic* will also have to be sought for; and even *silica* may be of importance—in the first instance because in the presence of much silica "explosive" properties of the pyrites must be feared (see p. 100), and secondly, in the case of cupreous pyrites, because silica lessens the value of the cinders. Even *silver* and *gold* are sometimes sought for (comp. Chem. News, xxvi. p. 63, xxxiv. pp. 94, 132, 152, 172); but it cannot be said that the quantities found have any influence on the commercial value of pyrites.

3. *Other Metallic Sulphides and spent Oxide of Gas Works.*

Pyrites proper has hardly any other application than that for sulphuric-acid making, and it is got almost exclusively for this purpose. In the case of cupreous pyrites the sulphur constitutes only a portion, but a very considerable one, of its value. The working of poor ores, such as those in question here, would not pay, apart from the noxious effect of the gas produced in calcining the ore, unless the price of the ore were very moderate; and this is only possible by the acid-makers paying on their part for the ore, which they can do very well, as most kinds of cupreous pyrites behave very well in the burners, and yield quite as much acid in proportion to their percentage of copper as the non-cupreous ores.

The case is different with most other sulphuretted ores occurring in smelting-operations, such as blende, galena, the many mixed ores containing these besides iron- and copper-pyrites, the richer copper-pyrites themselves, and, lastly, the intermediate products, "coarse metal," "matt," &c. These, for their metallurgical utilization, equally require a calcination evolving sulphurous acid; but the matter is very different here from what it is with a good pyrites, whether it be pure iron-pyrites or containing a few per cent. of copper. On the whole, all those ores and metallurgical products are much poorer in sulphur than ordinary good pyrites; and even for this reason they are less easily calcined in such a manner as to allow of utilizing the gas, because the evolution of heat by the combustion of their own sulphur is not sufficient to maintain the process energetically. An external stimulus was required before the smelting-works would seriously attempt to utilize the sulphurous acid contained in the gas from calcining the ores; and this was, the damage and nuisance caused by the *noxious vapour* all round the works. The claims for damages, the law-suits, and the measures taken by the authorities at last made it impossible in many places for the works to go on in the old way; and although it appeared at first as if the sulphurous acid could not be condensed at all in this case, or only at a loss, practice has now succeeded in fulfilling the task in most (but not in all) cases, principally by the construction of improved burners, which will be described in the chapter on that subject. To be sure, it would be too much to say that the task had been solved in all its parts; the success has mostly been only partial. In many cases where an ore could not possibly have been calcined so as to utilize the gas, mixing of it with others has been resorted to. Thus the Halsbrücke works, near Freiberg, roast galena and blende along with pyrites; and in 1870 they made 8000 tons of sulphuric acid from the gas. This properly so-called metallurgical sulphuric acid is principally made in Germany, much less in other countries.

Touching the sulphurous acid escaping as noxious vapour, Leplay (comp. Percy, 'Metallurgy,' 1862, i. p. 337) mentions that in South Wales annually 46,000 tons of sulphur escape into the air as sulphurous acid, along with arsenic, fluorine, lead, and zinc compounds, in spite of the condensing chambers. In fact the country round Swansea is deprived of all vegetation. At Freiberg the works in 1864 paid upwards of £2750 damages on account of their vapours; in 1870, after better condensation had been effected, only £239. It should not be left out of sight that sulphurous acid occurs in very large quantity, although in a much more dilute state, in all coal-smoke, and consequently in the atmosphere and the rain-water of all large towns, and that the most perfect "smoke-combustion" cannot do away with this. Much more injurious than the vapours escaping through high chimneys, which are soon diluted with air, is the smoke from brick-works, coke-ovens, and other fires which emit their smoke at a low height above the ground.

A detailed investigation of the influence of the noxious vapours at Freiberg on vegetation and on the health of domestic animals has been made by Freytag (abstracted in Wagner's 'Jahresb.' 1873, p. 180). The sulphurous acid, sulphuric acid, arsenic, and zinc vapours of the Freiberg smelting-works under unfavourable circumstances, even with the present condensing arrangements, may damage the vegetation of the neighbourhood in this way—that at a sufficient concentration they are taken up by the leaves covered with dew; on the evaporation of the water the organs affected are corroded and put into the same state as that into which they get by themselves when vegetation ceases. This injury can always be proved both by the eye and by chemical analysis. A "poisoning" of the soil or of the whole plant is out of the question. The assumption of an *invisible* injury done to the vegetation by the smelting-works' vapours and the awarding of damages founded hereon is unwarranted; it contradicts the fundamental principles of all exact investigation, and fosters the desire of the unreasoning multitude to incessantly raise fresh claims for damage alleged to have been done by the works. A decrease of the nutritive value of food-plants, in cases of visible injury done to the leaves, can only occur in consequence of the loss of these leaves and the lessened ability of the plants to decompose carbonic acid and produce organic matter therefrom. Any metallic oxides or salts adhering to the leaves of food-plants may become dangerous to the animal organization by inflammations of the mucous membranes, and, under very unfavourable circumstances, may produce death; but this fact can always be established with certainty by *post mortem* examination and by chemical analysis. The assumption that the "acid disease" occurring in that neighbourhood among the cattle, and tuberculosis, are produced by the noxious vapours is utterly unfounded and must be most decidedly contradicted.

Schroeder (Wagner's 'Jahresber.' 1874, p. 277) has made extensive experiments on the influence especially of sulphurous acid on vegetation, with results of which the following are the principal:—From air containing as little as $\frac{1}{1000}$ of its volume of SO_2 this gas is absorbed by the leaves of "leafy" (deciduous) trees and conifers; these retain it mostly, a smaller portion penetrating into the wood, the bark, and the leaf-stalks, either as such or after oxidation to sulphuric acid. Conifer-leaves absorb less sulphurous acid from the air for an equal surface of leaves than deciduous trees; the absorption takes place equally over the whole surface of the leaf, not by the stomates, and therefore has no relation to the number of the latter. A principal cause of the injurious effect of sulphuric acid is its causing a check to the normal evaporation of water, the disturbance being in a direct ratio to the quantity of SO_2; the evaporation is mostly affected by absorption of SO_2 in sunlight, at a high temperature and in dry air. Conifers are not visibly lowered in their transpiration by the same quantity of sulphurous acid which affects other trees (deciduous ones). The injury done by sulphurous acid is greater if the absorption takes place at the lower side, than if at the upper side.

Other communications on this matter, partly contradicting those of Schroeder, have been made by Stöckhart (Wagner, 'Jahresb.'

1874, p. 228). According to his observations at Zwickau, a distance of 630 metres (=690 yards) protects even the most sensitive vegetation against the effect of large volumes of vapours, if they escape through chimneys not less than 82 feet high. Conifers are much more sensitive than deciduous trees; the decreasing series of sensibility is—pine, pitch-pine, Scotch fir, larch, hawthorn, white beech, birch, fruit-trees, hazel-nut, horse-chestnut, oak, red beech, ash, linden, maple, poplar, alder, mountain-ash. In the parts of plants corroded by sulphurous acid, not this acid, but sulphuric acid can be found, and that to a larger extent than in the same parts of plants collected at the same time in districts free from smoke.

Fischer (Dingl. Journ. ccxx.) has given a short synopsis of the researches made in this field. We shall merely mention from it that, according to Hirt, the respiration of air containing 1, 2, 3, or even 4 per cent. of SO_2 has no sensible effect on health (?). Under special circumstances this sulphurous acid may even have a beneficial effect on public health by a disinfection of the air. What will be said further on upon this matter, in the chapter describing the condensation of hydrochloric acid, should also be compared.

In the following we shall enumerate the results obtained with the most important ores and metallurgical products. We shall, however, only speak of the utilization of their sulphurous acid for vitriol-making, omitting as outside our task any other attempted utilization, such as reduction to sulphur by red-hot coal, the formation of aluminium sulphate from clay-slate, &c. Unfortunately nothing like all the sulphur contained in those ores and products can be utilized as yet; and at Clausthal, for instance, latterly the condensation of the calcining vapours has been given up again, although here annually 1250 tons of sulphur are sent into the air, and the fir-woods of the neighbourhood are fearfully ravaged thereby.

Zinc-blende is calcined in several places with a view to sulphuric-acid making in the furnaces of Hasenclever and Helbig, perhaps also in others; by this no very rich gas is produced, but one still available in vitriol-making. The principal merit of having carried out the experiments consistently, and of having discovered the proper conditions for success, belongs to the Rhenania Works near Aachen, managed in succession by the two Hasenclevers (father and son). Already 25 years ago (comp. Hasenclever, *loc. cit.* p. 167) blende was roasted there in a reverberatory furnace with two divisions, the upper division being shaped as a close roaster, so that the gas could be taken to the lead chambers. The difficulty with blende is just this, that it is very difficult to desulphurize, or, rather, that the zinc sulphate formed is very difficult to decompose into zinc oxide, oxygen, and sulphurous acid. This is practically impossible with the heat produced in a muffle (close roaster); the ore incompletely roasted in the same must be desulphurized by an open fire, in which case the sulphurous acid, mixed with the fire-gas, cannot possibly be utilized. We have previously mentioned that a percentage of zinc in ordinary pyrites means almost certainly a corresponding loss of sulphur. But even the gas produced in the upper muffle is poor in SO_2, and in the chamber causes much loss of nitre and a bad yield of vitriol. A modification of the first furnace by Godin, as well as Gerstenhöfer's furnace, did not attain the end (Hasenclever, *loc. cit.* p. 168); it was not till 1870 that the problem was solved, by a combination of the old muffle-furnace with the shelf-furnace of Hasenclever and Helbig, which will be described in the 6th Chapter. This furnace is at work at Oberhausen, at Stolberg near Aachen, at Lethmathe near Iserlohn, at Rosdzin in Silesia, &c. The Stolberg blende contains about 25 per cent. of sulphur, of which 18 per cent. enters the chambers as SO_2, 6 per cent. escapes into the air, and 1 per cent. remains in the calcined mass. At Lethmathe calcareous blende with 32 per cent. of sulphur is worked, of which 20 per cent. is taken to the chambers as SO_2, 7 per cent. escapes with the fire-gas, and 5 per cent. remains as calcium sulphate (Stahlschmidt, in Hofmann's 'Official Report on the Vienna Exhibition,' i. p. 915). In this process as much coal is used as in the usual calcining process at zinc-works, viz. 28 parts to 100 of raw blende; the wages for roasting amount to 1*s*. 7*d*. per ton of blende more than with the ordinary reverberatory furnaces (see further details in the 6th Chapter).

At Freiberg a black kind of blende, mixed with pretty large quantities of pyrites, is used for vitriol-making, the lump ore being preliminarily roasted in large kilns. The cinders are then ground and the calcining finished in a reverberatory furnace without utilizing the sulphurous acid (Hasenclever, *loc. cit.* p. 169).

According to a German patent of Parnell's (No. 1351, 8th Sept. 1877) zinc sulphate is obtained by a preliminary calcination, dissolved in water, and so much raw blende mixed with it, that its zinc amounts to ⅓ of that in the sulphate; the mixture is dried, heated in a close furnace, and the SO_2 used in the well-known way. Under these circumstances a complete decomposition is said to take place below a red heat.

Copper pyrites and mixtures of this with blende, galena, &c. are roasted in several places in kilns so as to utilize the SO_2 in acid-chambers—at Chessy near Lyons, at Oker in the Harz, at Mansfield, at Swansea. At the Altenau silver-works near Clausthal in 1872, 228 tons of vitriol of 106° Tw. were made from copper-pyrites (and 314 tons from lead-matts, Wagner's 'Jahresb.' 1874, p. 276). At Freiberg the Mulden and Halsbrücke works proceed in the same way; but they only utilize the ores and products pretty rich in sulphur for vitriol-making.

At Oker (Bräuning, 'Zeitschr. f. Berg- Hütten- u. Salinenwesen im preuss. Staate,' 1877, p. 132) at present about 15,000 tons of ore per annum are used for acid-making, viz. the five following kinds:—

1.	Iron-pyrites about	2500 tons.
2.	Ordinary copper-pyrites	4200 „
3.	Mixed ores	3350 „
4.	Rich copper-ores, excluding those richest in copper	750 „
5.	Lead-ores containing pyrites	4200 „

The average composition of the ores Nos. 2 to 5 is shown in the following Table:—

	Lead-ores.	Mixed ores.	Rich copper-ores.	Ordinary copper-ores.
Cu	0·55	5·06	15·66	7·90
Pb	11·79	9·52	4·88	2·17
Ag	0·016	0·016	0·017	0·01
Fe	11·86	16·26	25·32	34·93
Zn	23·86	18·99	7·90	3·71
Mn	2·18	1·75	1·64	1·08
Co+Ni	0·04	0·06	0·04	0·08
As+Sb	0·12	0·12	0·10	0·08
SiO_2	1·06	1·53	0·87	1·70
Al_2O_3	1·81	2·02	0·94	2·61
$CaCO_3$	3·72	1·91	2·21	2·32
$MgCO_3$	0·89	0·56	0·42	0·74
$BaSO_3$	15·97	13·77	6·66	0·63
S	25·00	27·18	32·89	41·08
Total	98·866	98·746	99·547	99·04

Traces of Hg, Tl, Cd, and Se have been found both in the ores and in the products obtained therefrom.

Apart from pure pyrites, the "ordinary ores" are best adapted for vitriol-making, because they contain their sulphur mostly as FeS_2; the "mixed ores" are less favourable, on account of their galena, and the rich copper-ores on account of their large percentage of copper. Of the lead-ores only those amply permeated by pyrites are fit for vitriol-making. The sulphur in the ores worked at Oker varies from 20 to 40 per cent.; on an average it is 30 per cent.; but it must be noticed that the sulphur of the galena is altogether unavailable for vitriol-making. The case is not much better when copper-pyrites predominates, because this furnishes too poor a gas, and, moreover, decrepitates and falls to powder in roasting. If no more than 35 per cent. of copper-pyrites is mixed with iron-pyrites, it does no harm. Blende behaves in a similar way, but rather more favourably; ores containing 35 per cent. blende along with 25 per cent. pyrites yield gas quite adapted for vitriol-making.

The first sulphuric-acid works at Oker were erected in 1841; now there is there the largest production of vitriol in Germany, viz. 14 sets of chambers with a capacity of 800,000 cubic feet.

Galena is probably nowhere worked in such a way as to get out its sulphur in the shape of sulphuric acid. The purest galena contains only 13·4 per cent. of sulphur; it is transformed into lead sulphate on roasting, and only in the strongest white heat gives off a portion of its sulphur as SO_2; moreover the metallurgical processes to which it is subject are of such a nature that only poor gas can be produced from it. This matter has been discussed by Bode in his 'Beiträge zur Theorie und Praxis der Schwefelsäurefabrikation,' 1872, pp. 32 & 63; his conclusion is that even mixtures of galena and pyrites cannot be roasted in kilns for vitriol-making if they contain more than 18 to 20 per cent. of galena.

"*Coarse metal*" of copper-smelting is roasted for vitriol at Mansfeld. A product containing 34 per cent. Cu, 28 per cent. Fe, and 28 per cent. S, according to Bode, yields gas with 5½ per cent. by volume of SO_2, and at a sufficiently high temperature to work with the Glover tower. In most cases, up to the present, coarse metal cannot be roasted so as to utilize the SO_2.

Lead-matt is used for vitriol-making—for instance, at Freiberg and in the Lower Harz; it is roasted there in large kilns of 12½ tons capacity. The matt loses half its sulphur, and yields gas with

4 to 6 per cent. of SO_2; the temperature, according to Bode, is high enough for the Glover tower. In the Upper Harz, the utilization of its sulphur in metallurgy has in general not been found practicable.

The spent oxides from the purification of *gas* by hydrated ferric oxide are in many places used for vitriol-making. This sulphur originally also comes from pyrites, viz. from that contained in the coal, which appears in the gas mostly as sulpuretted hydrogen. Most large works remove it, according to the patent of F. C. Hills (1857), by a mixture of hydrated iron oxide and sawdust. In this case sulphide of iron and sulphur are formed, according to the equation

$$Fe_2(OH)_6+3\,H_2S=2\,FeS+S+6\,H_2O\,;$$

and when the mass, having become inactive, is exposed to the air, it again passes over into ferric hydroxide, more sulphur being precipitated, thus,

$$2\,FeS+O_3+3\,H_2O=Fe_2(OH)_6+S_2.$$

The hydroxide thus reproduced and mixed with sulphur is again used in the purifiers, and thus regenerated about 30 or 40 times before the sulphur has accumulated therein to such an extent that the mixture does not work any more; it is then replaced by fresh oxide, and the spent ore is passed over to vitriol-makers.

Phipson states the composition of such a mass to be :—

Water	14	per cent.
Sulphur	60	„
Organic substance insoluble in alcohol	3	„
Organic substance soluble in alcohol (calcium ferrocyanide and sulphocyanide, ammonium sulphocyanide, salammoniac, hydrocarbons)	1·5	„
Clay and sand	8	„
Calcium carbonate, ferric oxide, &c.	13·5	„
	100	„

Hot water extracts the ferrocyanides and sulphocyanides, along with salammoniac; the solution can be evaporated to dryness, and the residue separated by alcohol into insoluble calcium ferrocyanide and soluble sulphocyanides and salammoniac.

According to the Analyses of Davis ('Chemical News,' xxix. 1874, p. 30), 3 samples of spent oxides contained:—

	I.	II.	III.
Sulphur	64·376	62·358	67·956
Ferric hydroxide	14·421	17·112	15·335
Insoluble	11·052	5·099	8·304
Moisture............................	2·079	5·387	3·900
Lime (as CaS)	2·399	......	......
Sawdust	2·470	1·776	1·002
Calcium carbonate	......	5·135	3·006
Ammonium sulphocyanide	2·662	1·324	1·102
Ammonium chloride............... Ammonium cyanide	0·605	......	......
Ammonium ferrocyanide	......	1·663	......
Prussian blue	trace	0·366	trace
	100·064	100·220	100·605

These samples seem to have been taken from precipitated iron hydroxide, to judge from further analyses by Davis (Chem. News, xxxvi. p. 189), in which also tarry substances are taken into account.

Residues proceeding from

	Precipitated $Fe_2(OH)_6$.	Bog-iron-ore.	Copperas.	Bad oxides.
Ferric hydroxide	17·74–19·36	15·96–26·42	5·04– 6·84	8·72–20·40
Sawdust	1·98– 4·72	1·14– 3·72	1·04– 3·24	2·16– 9·76
Calcium carbonate..............	0· – 1·04	0· – 1·73	0·	0· –10·36
Ammonium sulphocyanide ...	1·99– 2·74	0·94– 1·93	1·98– 3·41	1·18– 4·72
Ammonium ferrocyanide	trace	trace– 0·21	0·27– 0·64	trace– 0·44
Tarry matters.....................	0·72– 1·22	0·92– 1·14	0·72– 1·18	0·55– 1·04
Sulphur	62·44–67·18	48·76–57·44	48·76–55·74	32·42–42·16
Insoluble in dilute HCl	3·66– 5·47	9·74–11·42	7·82–12·68	12·12–20·71
Prussian blue.....................	....	trace– 0·17	trace– 1·74	trace– 0·64
Calcium sulphate	....	....	trace– 1·43	0· – 3·23
Ammonium sulphate............	....	....	12·78–16·72	0· – 1·14
Moisture (by difference)	4·72– 5·76	7·22–10·82	7·98– 9·22	7·49–33·41

From these analyses it can be seen, first, that it is decidedly best to extract the mass at first with water, in order to remove the ammonia compounds, which are in themselves valuable, and which, if they get into the chambers, destroy a good deal of nitre (their value is certainly greatly lessened by the sulphocyanide); secondly, that sometimes a considerable quantity of calcium carbonate is present, which may get into it at the gas-works by lime being added, on purpose or by mistake, and which, of course, retains an equivalent quantity of sulphur in the shape of gypsum. In fact a sample of the residue left after burning contained

Insoluble	33·386
Ferric oxide	52·399
Calcium sulphate	13·315
Sulphur	0·200

These impurities (which cause a loss by retaining sulphuric acid) and the sulphates present from the first (which are not available) must be allowed for in analyzing. This, according to Davis, was formerly done by extracting the sulphur by means of carbon bisulphide, evaporating the solution, and weighing off the sulphur; but as the presence of tarry matters causes an error, Davis now makes the analysis by burning the sulphur in a current of air in a combustion-tube of Bohemian glass, conducting the SO_2 formed into an absorbing apparatus filled with iodine solution, and retitrating the unaffected iodine by a solution of sodium hyposulphite (Chem. News, xxxvi. p. 190).

The burning of this gas-sulphur is usually done in shelf-furnaces similar to those used for pyrites smalls. They will be described in detail further on. Already in 1861, at Barking Creek, on the Thames, 2180 tons of this material was used; but much larger quantities might have been got, since, according to A. W. Hofmann ('Report,' 1862, p. 15), even at that time at least 10,000 tons of sulphur were contained in the London gas.

In France also, at that time, the sulphur from gas-works was used on a large scale. The factory at Aubervilliers, belonging to the Society of St.-Gobain, used no other; Messrs. Seybel and Co. at Liesing, near Vienna, and Kunheim and Co. at Berlin (Wagner's Jahresb. 1864, p. 153; Hasenclever, *l. c.* p. 167) do the same.

At Kunheim's works in Berlin the spent oxides are utilized in a very rational manner. First, by washing, the ammonia salts are extracted; the residue, boiled with a little lime, yields a double cyanide, from which, by the addition of potassium sulphate, a solution of potassium ferrocyanide is obtained; the new residue, dried and roasted, yields SO_2 for the acid-chambers; and there remains behind an oxide of iron applicable for purifying the gas (Kopp, 'Swiss Report on the Vienna Exhibition,' iii. p. 31). *Cal-*

cined iron oxide will, however, hardly be fit for the purification of gas.

O. Schott (Dingl. Journ. ccxxi. p. 142) has proposed *to utilize, for vitriol-making, the sulphurous acid given off in making glass from sodium sulphate.* The gas is to be made richer in sulphur by employing for the glass-mixture gypsum in lieu of limestone. Sulphate of soda, gypsum, and coal are to be mixed in proper proportions, and brought to a bright red heat in muffle-furnaces or in elliptical glass pots, until the SO_2 is driven off. The fritted residue of sodium and calcium silicate is to be powdered and used by glass-works; the gas is to be conducted into lead chambers and worked for vitriol. This process seems entirely impracticable, especially since such diluted gas (mixed with a great deal of carbonic acid) has not yet been utilized.

4. *Nitrate of Soda,*

NO_3Na.

$\frac{1}{2}$ (Na_2O)	= 31	36·47	per cent.
$\frac{1}{2}$ (N_2O_5)	= 54	63·53	„
	85	100·00	

Hardness 1·5 to 2; spec. grav. 2·09 to 2·39. In the pure state, and in large crystals, it is colourless, transparent, and brilliant as glass; in small crystals it is white and opaque. It has a cooling, bitter taste. Heated to a certain temperature, it melts; at a red heat it is decomposed into sodium nitrite and oxygen gas. Mixed with coal, it deflagrates on heating. It attracts moisture from the air (especially if not quite free from chlorides), and readily dissolves in water, with a considerable lowering of the temperature.

1 part of sodium nitrite, according to Marx, requires for solution 1·58 part of water at −6°, 1·25 at 0°, 0·46 at +119° C. According to Kopp, 1 part of sodium nitrite at 18°·5 C. requires 1·14 of water, or 100 parts of water dissolve 87·72 parts of the salt. In the presence of sodium chloride its solubility is considerably less.

Specific Gravity of the Solutions of Sodium Nitrate at 20° C.

Parts of salt in 100 water.	Specific gravity.	Parts of salt in 100 water.	Specific gravity.
1	1·0065	26	1·1904
2	1·0131	27	1·1987
3	1·0197	28	1·2070
4	1·0264	29	1·2154
5	1·0332	30	1·2239
6	1·0399	31	1·2325
7	1·0468	32	1·2412
8	1·0537	33	1·2500
9	1·0606	34	1·2589
10	1·0676	35	1·2679
11	1·0746	36	1·2770
12	1·0817	37	1·2863
13	1·0889	38	1·2958
14	1·0962	39	1·3055
15	1·1035	40	1·3155
16	1·1109	41	1·3255
17	1·1184	42	1·3355
18	1·1260	43	1·3456
19	1·1338	44	1·3557
20	1·1418	45	1·3659
21	1·1498	46	1·3761
22	1·1578	47	1·3864
23	1·1659	48	1·3968
24	1·1740	49	1·4074
25	1·1822	50	1·4180

Sodium nitrate crystallizes from its solutions in rhombohedric crystals with angles of 106° 30′ and 73° 30′. Its melting-point is 316°–319° C. (Carnelley, Journ. Chem. Soc. 1878, ii. p. 277).

It occurs in many places in small quantities; but the only large bed of it is in the south of Peru, near the frontier of Chili, in the district of Tarapaca, between 19 and 23½ degrees of south latitude, partly in the plateau of Atacama, 3300 feet above the sea-level, and covering 260,000 acres. It was discovered in 1821 by Mariano de Rivero, and has been worked since 1830. According to G. Langbein (Wagner's Jahresb. 1871, p. 300, and 1872, p. 290) there existed in 1871 in this district eleven large nitre-refineries, with a daily production of about 300 tons refined nitre. The nitre-bearing rock, called *caliche,* is found in layers of from 10 inches to 5 feet depth, which rarely crop out at the surface. The overlying rock, called *costra,* is 18 inches to 7 feet thick, and consists principally of a hard conglomerate of sand, felspar, phosphates, and other minerals.

The composition of the caliche varies; it contains from 48 to 75 per cent. of sodium nitrate, 20 to 40 per cent. of sodium chloride, and varying quantities of sodium sulphate, calcium sulphate, potassium nitrate, potassium iodate, magnesium chloride, also insoluble earthy portions and organic substance (guano). It is first broken by a stone-breaking machine, and then put into the dissolvers. These are partly open square tanks, preferably, however, closed egg-shaped boilers with two man-holes—one on the top for filling in the caliche, another at the bottom for emptying the residue. The mass rests on a perforated bottom. The boilers are filled entirely with the broken rock, and half with mother liquor, and are heated by direct steam injected below the false bottom. After 1¼ to 2½ hours the liquid, then sufficiently saturated with nitre, is run into settlers; from these it flows, after several hours, into a second settler, where, by half an hour's rest, it allows some still-suspended common salt to subside, and then runs into shallow coolers. The residue from the dissolvers, which still contains 15 to 35 per cent. of sodium nitrate, is either emptied at once or boiled once more with fresh water. The crystals, separated in the coolers after draining off the mother liquors, are spread in layers of 12 to 18 inches thickness on a large surface exposed to draught, and dried with frequent stirring. The total cost of sodium nitrate, up to its reaching European ports, in 1871, amounted to £8 18*s.* per ton, which leaves a good margin for profit at the average price of £12 (it has reached £16 and more). Most nitrate is shipped from Iquique.

Its exportation is constantly increasing, as is proved by the following figures:—

	tons.
1830	935
1835	7020
1840	11368
1850	25592
1860	68512

	tons.
1870	147170
1871	180295
1872 ......exceeding	200000

Since July 12th, 1873, the Peruvian Government has taken in hand the sale of nitrate of soda, and has fixed the maximum exportation at 225000 tons.

Touching the formation of nitrate of soda, the hypothesis of C. Nöllner (Wagner's Jahresb. 1868, p. 290) is considered most probable, according to which enormous masses of seaweed have been thrown by hurricanes into that bay, at that time situated at a much lower level, the nitrogen of the seaweed, on its slow decay, occasioning the formation of caliche. In favour of this hypothesis are the constant occurrence of iodine in the caliche, the prevalence of westerly winds in that country, the total absence of rain, so that the nitre formed was not washed out, and the well-known gradual rising of the whole coast above the sea-level.

The iodine collecting in the mother liquors in the shape of iodate is obtained as such, or in the form of cupreous iodide, in a few works, and shipped to Europe.

A few analyses may be subjoined here:—

	Caliche.				Costra.
	a.	*b.*	*c.*	*d.*	*e.*
Sodium nitrate	70·62	60·97	51·50	49·05	18·60
Sodium iodate	1·90	0·73	...	...	...
Sodium iodide	...	...	traces	traces	...
Sodium chloride	22·39	16·85	22·08	29·95	33·80
Sodium sulphate	1·80	4·56	8·99	9·02	16·64
Potassium chloride	...	...	8·55	4·57	2·44
Magnesium chloride	...	...	0·43	1·25	1·62
Magnesium sulphate	0·51	5·88	...	...	...
Calcium sulphate	0·87	1·31	...	...	...
Calcium carbonate	...	...	0·12	0·15	0·09
Silica and ferric oxide	...	...	0·90	2·80	3·00
Insoluble	0·92	4·06	6·00	3·18	20·10
Moisture	0·99	5·64	...	...	...
	100·00	100·00			

The analyses *a* and *b* (*a* white, *b* brown caliche) are by Machattie (Chem. News, xxxi. p. 263). They are somewhat suspicious, both on account of the total absence of potassium salts and of the extremely improbably high percentage of sodium iodate. This is all the more noticeable as Machattie at the same time states the average percentage of iodine in five samples of *mother liquor* to be $=0{\cdot}56$, equal to 0·873 per cent. of sodium iodate, which may be nearer the truth. The analyses *c*, *d*, and *e* are by V. L'Olivier (Compt. Rend., 26th October, 1875).

R. Wagner (Jahresb. 1869, p. 248) found in commercial nitrate of soda

Sodium nitrate	94·03
„ nitrite	0·31
„ chloride	1·52
Potassium chloride	0·64
Sodium sulphate	0·92
„ iodate	0·29
Magnesium chloride	0·93
Boric acid	traces
Moisture	1·36
	100·00

The nitrate of soda imported into England, as used by vitriol-makers, is much purer than the above sample. The English sellers mostly guarantee a maximum of 5 per cent. "refraction" (that is, the total percentage of all foreign constituents, inclusive of water), frequently, however, 4 or even 3½ per cent. refraction. English vitriol-makers would, indeed, altogether refuse nitrate containing upwards of 3 per cent. of chlorides, like that analyzed by Wagner, 1 per cent. being the maximum allowed. The muriatic acid generated from them, of course, gives, with nitric acid, free chlorine and its compounds with nitrogen oxides, and causes a loss of the latter. The average composition of nitrate for chemical works is

96 sodium nitrate (including nitrite, iodate, &c.),
0·5 chlorides (calculated as NaCl),
0·75 sulphates (calculated as $NaSO_4$),
2·75 moisture.

In the factories the value of nitrate is mostly only estimated indirectly, viz. the "refraction." 10 grams are well dried in a porcelain capsule, weighed again, dissolved, the residue (if any) estimated, the liquid dissolved to a certain volume, and, in certain portions of the liquid, chlorine and sulphuric acid estimated in the usual way. Of course a direct estimation of the nitric acid can be made by one of the methods described on page 48 &c.

When *emptying nitrate of soda from the bags*, a certain quantity of the salt, which is always damp, remains adhering to them—which not only causes loss, but makes them useless, and even produces a danger of fire. It is therefore well to lixiviate the bags with hot water, and to dry them. The solution is evaporated to a small bulk and crystallized.

The mother liquor is always very rich in chlorides, which seems to show that the deliquescence of sodium nitrate is not a property of the pure salt, but is owing to the magnesium and calcium chloride contained in it, since the dampest salt will adhere to the bags.

5. *Nitric Acid,*

NO_3H.

This may also be called one of the raw materials of vitriol-making, although a manufactured product itself, in those works using it in lieu of solid nitre.

Its properties and mode of manufacture need only be described here very briefly, especially as it is nowhere in Great Britain used for the purpose of vitriol-making.

The nitric acid proper (the monohydrate) has the equivalent 63, and may be said to contain as constituents 85·71 nitric anhydride (N_2O_5) and 14·29 water. Its specific gravity is 1·54 at 20°, or 1·55 at 15°. It is colourless if perfectly pure; but the strongest acid of commerce is always coloured yellow, or even red, by a partial decomposition into oxygen and nitrogen tetroxide, N_2O_4 (hyponitric acid). Its boiling-point is 86° C. On boiling an acid containing a little water, at first strong acid distils over, till the boiling-point of the remainder has reached 126°, at which point the thermometer remains stationary, and an acid of constant composition for any certain pressure distils over. Exactly the same point is reached from the opposite side by distilling more dilute acids, in which case water distils over, and the remaining acid becomes more and more concentrated, till the above stationary point is reached. The acid at that point has nearly the composition $2\,NO_3H + 3\,H_2O$ (corresponding to $60\,N_2O_5$ and $40\,H_2O$) and a specific gravity of 1·42.

The oxidizing properties of nitric acid are well known, and cannot be described in detail here; but it should be mentioned that an acid containing a large proportion of the lower oxides of nitrogen, the "red fuming nitric acid," has even more strongly oxidizing properties than the pure acid, because this helps to explain some points in the theory of the formation of sulphuric acid, as we shall see in the respective chapter.

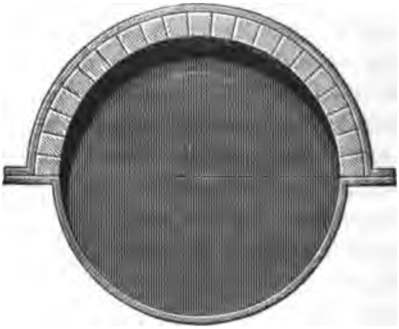
Nitric acid has been known since the time of Geber, in the 8th century; and Raymundus Lullus in 1225 taught how to prepare it by distilling a mixture of clay and saltpetre. Now-a-days it is always made by distilling nitrate of soda with sulphuric acid, an excess of the latter acid beyond the theoretical quantity having to be used in practice.

In theory 85 parts of $NaNO_3$ require 49 parts of SO_4H_2, and yield $63 NO_3H$ along with $71 Na_2SO_4$; this comes to the same as 57·6 parts of SO_4H_2, or, say, 60 parts of ordinary strong oil of vitriol (with 93 per cent. of SO_4H_2) to 100 parts of 95-per-cent. nitrate. If these proportions are used, a portion of the nitric acid is always decomposed into O and N_2O_4, and red fuming acid is obtained. To avoid the loss involved in this operation, generally more dilute nitric is produced by employing weaker sulphuric acid, say of 140°–148° Tw., and more than the theoretical quantity of it, generally from 20 to 30 per cent. in excess of the simple equivalent. In this case the admixture of a certain quantity of sodium bisulphate makes the residue of distillation much more easily fusible, and facilitates its removal from the retorts. When the acid is made at works where salt is decomposed, even more sulphuric acid than the above is generally employed, as the excess is not lost, the residual "cylinder-cake" or "nitre cake" being regularly mixed with the salt to be decomposed in the sulphate-pans; in this case as much sulphuric acid is saved as corresponds to the bisulphate contained in the cylinder-cake.

The manufacture of nitric acid takes place in very similar apparatus to those formerly used in the manufacture of muriatic acid, where the latter was the principal product, and which we shall describe in the second book, viz. glass retorts or cast-iron retorts. The former are very little used now on a large scale. The retorts in most works are cylindrical, generally about 2 ft. wide and 5 ft. long, two being heated by the same fire. The ends of the cylinders are free; one of them is fixed and provided with a pipe for taking away the vapours; the other end takes off and serves for charging the nitre and discharging the residue. A hole and S-shaped funnel in the man-lid allow of running in the sulphuric acid. These cylinder-ends cause a good deal of cooling, and consequently a loss of fuel, which can be avoided to a great extent if they are not made of iron but of a single stone flag each; the charging end also remains fixed in this case, the nitre being charged through a small general opening in it, and the residue being run off in a liquid state through a pipe generally closed by a ground-in iron stopper. A little more sulphuric acid is employed in this case, so as to obtain a very fluid mass at the end. If the sulphuric acid is taken at 144° Tw., the receivers will contain a nitric acid of 77° to 82° Tw.; if weaker acid is desired, a little water is put into the receivers. The strongest acid, of 106° Tw., can only be made from strong vitriol and dried nitrate.

The cylinders are often cast so that their upper half can be protected against the attack of the acid by lining it with acid-proof bricks (see fig. 9); but according to some this does more harm than good, as the upper part of the metal cylinder is all the less acted upon by the nitric acid the hotter it becomes.

Fig. 9.



Some works use large semicylindrical troughs of cast metal with broad flanges and a vertical rim all round, in order to cover them by a brick arch or a stone slab.

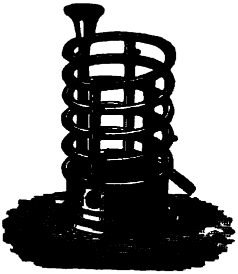
Many continental works use retorts of a very different shape, viz. cast-iron pots about 4 ft. high and equally wide, having an opening with a lid at the top for introducing nitre and sulphuric acid, and a side branch for taking away the gas, similar to a laboratory-retort. The whole is set in a furnace in such a way that it is altogether surrounded by the fire, even at the top, to which access is obtained from time to time by removing a fire-clay slab forming a temporary cover to the furnace in that place. This arrangement saves a good deal of fuel; and as the metal gets hot all over, the retort stands very well. The melted residue remaining after each operation is sometimes run off by a side branch at the bottom, closed by a plug; but more frequently it is taken out with ladles from the top whilst still in the liquid state. Each of these apparatus holds 5 cwt. of nitre; and each operation lasts 14 or 16 hours.

The condensing-apparatus always consists of stoneware Woulfe's bottles, exactly like those used for muriatic acid (compare that chapter), combined in sets of seven to nine or even more. According to the strength of acid intended to be made, they are either left empty or charged with a little water, as already mentioned. Sometimes they are cooled on the outside with water; but generally this is not the case. Each of them is provided with a bottom tap for running off the condensed acid; that from the first two receivers is more impure than that of the others, as it contains a little sulphuric acid and iron carried over from the retort. The acid becomes weaker the further the receivers are from the retort. Since the receivers now and then crack with the heat, it is advisable to put them on stoneware saucers provided with a spout, for collecting the acid running out.

The cement for the temporary connexions is mostly made of clay and horsedung, or something of that kind. For luting the arms into the receivers &c. the following cement is said to serve very well:—$\frac{1}{2}$ ounce of finely powdered brimstone is shaken up with 5 lb. of hot linseed oil; 1 lb. of cut-up india-rubber scrap is added, and the whole boiled with constant stirring till it is all dissolved or converted into a homogeneous mass. After cooling, the mixture is mixed with finely ground sulphate of barytes, and worked up in an iron mortar, till it forms a tough homogeneous mass. This cement both resists the acid and preserves a certain degree of elasticity.

Several small but not unimportant improvements have latterly been effected in the apparatus for condensing the nitric acid. Instead of allowing the acid vapours to pass directly into the first

Fig. 10.

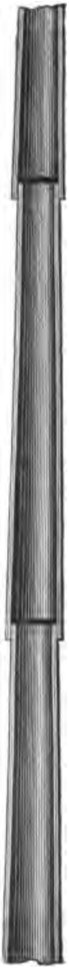


receiver, which even with the best ware often leads to breakages, owing to the sudden change of temperature, especially with forced working, latterly the vapours are previously cooled in different ways. Sometimes stoneware worms cooled by water are employed, of the shape of fig. 10, as supplied by Messrs. Doulton and Watts, of Lambeth, and other firms; they are very efficient, and stand changes of temperature very well.

A cheaper arrangement of Göbel's (Dingl. Journ. ccxx. p. 241) has also been very successful. This is a straight glass tube, bent at each end, lying in cold water; for each ton of nitre 4½ tons of cooling-water are required. One end of the glass tube is loosely connected with the glass tube coming out of the retort; the other end enters the first receiver. With the aid of this simple apparatus the quantity of nitre decomposed per 36 hours can be raised from 5 cwt. to 6 cwt.; or the 5 cwt. can be decomposed by fractional distillation, so that colourless acid is obtained in the first operation; this is done by means of a two-way cock. Besides, the receivers can be diminished by two thirds, from 9 to 3, as most of the acid is already condensed in the glass tube and collects in the first receiver, in which thus an extremely concentrated acid can be obtained—for instance, in the first receiver nearly 3 cwt. of 1·53 spec. grav., in the second about 1 cwt. of 1·49 spec. grav., in the third acid of 1·32. With this apparatus no receivers are ever cracked, and the glass tube lasts six months, each renewal costing about 5*s*. Göbel states the usual breakage per month and apparatus as 5 receivers, or 60 receivers per annum at £1 each; but many works have much less breakage. Lastly, according to Göbel, the old yield from 100 parts of pure sodium nitrate is 125·3 parts nitric acid of 1·33 spec. grav., but with his apparatus 132·1 parts, equal to 4·75 per cent. increase. On the other hand, the cost of pumping the cooling-water must not be forgotten.

Much simpler, again, but not quite so efficient as Göbel's apparatus, is the interposition of glass tubes with *cooling by the air only* between the retorts and the receivers. In this case not only the cooling-water is saved, but it is possible to employ the tube in several pieces of a somewhat conical shape, loosely put together (fig. 11); only the whole must have enough fall for the condensed acid not to stop in the tubes and run out of the joints. With a length of from 10 to 13 feet (the longer the better) the cooling by air is already very efficient.

Fig. 11.



Further, a contrivance is frequently met with for depriving the gas issuing from the last receiver of all not condensed nitrogen oxides before they enter the chimney. This is a small Gay-Lussac's absorbing tower (compare Chapter X.), consisting of a stack of stoneware pipes filled with coke and continually fed with sulphuric acid of 144° to 152° Tw.; the gas enters at the bottom and issues at the top, and thereby gives up all its nitrous and hyponitric acids to the vitriol, which arrives at the bottom as a more or less rich "nitrous vitriol," and can be employed in the manufacture of sulphuric acid. For a ton of nitre from 3½ to 4 cwt. of vitriol are required; and nitrogen acids corresponding to 3 or 5 per cent. of nitric acid of 1·33 spec. grav. are absorbed by the same, more or less, according to the percentage of chlorides in the nitre.

For such manufactures of nitric acid as are not in connexion with sulphuric-acid works, it is preferable to feed the coke-tower with water. If care is taken that there is always an excess of air present, not merely the last remnant of nitric acid is condensed, but the hyponitric acid is likewise converted into nitric acid and thus saved. The same reaction is already used in several other cases in order to reconvert the lower nitrogen-acids, previously lost, into nitric acid. But this does not act as thoroughly as the absorption by strong vitriol; a little hyponitric acid &c. is always lost; and therefore the proposals of R. Wagner (igniting nitre with alumina), Walz (heating nitre with calcium carbonate and steam in retorts), Kuhlmann (heating nitre with manganese chloride, manganese dioxide, common salt and nitrogen tetroxide being formed), and others have not been ultimately successful.

The *refining* of nitric acid consists in driving off the lower oxides, so that the acid is got colourless. This can be done by long heating in a water-bath, which is a tedious operation—much more quickly if a current of air is blown through the gently heated acid; the air along with the gas contained in it is conducted through a small coke-tower fed with water, where dilute nitric acid is obtained. There is, however, a little loss in that operation. This refining is, of course, unnecessary for nitric acid used in the manufacture of sulphuric acid.

The following is a table of *the percentage of nitric acid for different specific gravities*, according to Kolb (Bull. Soc. Ind. de Mulhouse, 1866, p. 412) :—

Degrees (Baumé).	Spec. gravity.	100 parts contain at 0° C.		100 parts contain at 15° C.	
		NO_3H.	N_2O_5.	NO_3H.	N_2O_5.
0	1·000	0·0	0·0	0·2	0·1
1	1·007	1·1	0·9	1·5	1·3
2	1·014	2·2	1·9	2·6	2·2
3	1·022	3·4	2·9	4·0	3·4
4	1·029	4·5	3·9	5·1	4·4
5	1·036	5·5	4·7	6·3	5·4
6	1·044	6·7	5·7	7·6	6·5
7	1·052	8·0	6·9	9·0	7·7
8	1·060	9·2	7·9	10·2	8·7
9	1·067	10·2	8·7	11·4	9·8
10	1·075	11·4	9·8	12·7	10·9
11	1·083	12·6	10·8	14·0	12·0
12	1·091	13·8	11·8	15·3	13·1
13	1·100	15·2	13·0	16·8	14·4
14	1·108	16·4	14·0	18·0	15·4
15	1·116	17·6	15·1	19·4	16·6
16	1·125	18·9	16·2	20·8	17·8
17	1·134	20·2	17·3	22·2	19·0
18	1·143	21·6	18·5	23·6	20·2
19	1·152	22·9	19·6	24·9	21·3
20	1·161	24·2	20·7	26·3	22·5
21	1·171	25·7	22·0	27·8	23·8
22	1·180	27·0	23·1	29·2	25·0
23	1·190	28·5	24·4	30·7	26·3
24	1·199	29·8	25·5	32·1	27·5
25	1·210	31·4	26·9	33·8	28·9
26	1·221	33·1	28·4	35·5	30·4
27	1·231	34·6	29·7	37·0	31·7
28	1·242	36·2	31·0	38·6	33·1
29	1·252	37·7	32·3	40·2	34·5
30	1·261	39·1	33·5	41·5	35·6
31	1·275	41·1	35·2	43·5	37·3
32	1·286	42·6	36·5	45·0	38·6
33	1·298	44·4	38·0	47·1	40·4
34	1·309	46·1	39·5	48·6	41·7
35	1·321	48·0	41·1	50·7	43·5
36	1·334	50·0	42·9	52·9	45·3
37	1·346	51·9	44·5	55·0	47·1
38	1·359	54·0	46·3	57·3	49·1
39	1·372	56·2	48·2	59·6	51·1
40	1·384	58·4	50·0	61·7	52·9

TABLE (continued).

Degrees (Baumé).	Spec. gravity.	100 parts contain at 0° C.		100 parts contain at 15° C.	
		NO_3H.	N_2O_5.	NO_3H.	N_2O_5.
41	1·398	60·8	52·1	64·5	55·3
42	1·412	63·2	54·2	67·5	57·9
43	1·426	66·2	56·7	70·6	60·5
44	1·440	69·0	59·1	74·4	63·8
45	1·454	72·2	61·9	78·4	67·2
46	1·470	76·1	65·2	83·0	71·1
47	1·485	80·2	68·7	87·1	74·7
48	1·501	84·5	72·4	92·6	79·4
49	1·516	88·4	75·8	96·0	82·3
49·5	1·524	90·5	77·6	98·0	84·0
49·9	1·530	92·2	79·0	100·0	85·71
50·0	1·532	92·7	79·5		
50·5	1·541	95·0	81·4		
51·0	1·549	97·3	83·4		
51·5	1·559	100·0	85·71		

The following Table, showing the *increase of the specific gravity of nitric acid on cooling down to* 15° C., has been published by Göbel (Dingl. Journ. ccxx. p. 244) :—

Temperature C.	Increase on cooling to 15° C.	Temperature C.	Increase on cooling to 15° C.	Temperature C.	Increase on cooling to 15° C.
°	° Baumé.	°	° Baumé.	°	° Baumé.
45·0	3·65	35·0	2·10	25·0	0·90
44·5	3·56	34·5	1·98	24·5	0·80
44·0	3·48	34·0	1·92	24·0	0·76
43·5	3·40	33·5	1·85	23·5	0·72
43·0	3·32	33·0	1·79	23·0	0·67
42·5	3·23	32·5	1·73	22·5	0·63
42·0	3·15	32·0	1·67	22·0	0·59
41·5	3·08	31·5	1·62	21·5	0·55
41·0	3·00	31·0	1·56	21·0	0·52
40·5	2·92	30·5	1·50	20·5	0·48
40·0	2·85	30·0	1·45	20·0	0·45
39·5	2·73	29·5	1·34	19·5	0·36
39·0	2·65	29·0	1·29	19·0	0·33
38·5	2·58	28·5	1·23	18·5	0·29
38·0	2·50	28·0	1·18	18·0	0·25
37·5	2·43	27·5	1·13	17·5	0·20
37·0	2·36	27·0	1·08	17·0	0·13
36·5	2·29	26·5	1·03	16·5	0·07
36·0	2·23	26·0	0·99	16·0	0·05
35·5	2·16	25·5	0·94	15·5	0·02

Apart from the nitric acid made specially for this purpose, latterly vitriol-manufacturers have also used largely the mixture of nitric acid with much strong sulphuric acid which is obtained in aniline-works in the manufacture of *nitrobenzine,* in dynamite works in the manufacture of *nitroglycerine,* and in other analogous cases. Only, as a matter of course, especially in the case of acid from nitroglycerine, all drops of oil must be rigidly kept away. These acids may be used in the Glover tower or in the steam-columns (Chapter X.).

CHAPTER V.

THE PRODUCTION OF SULPHUROUS ACID FROM BRIMSTONE.

ALREADY in the historical part attention has been drawn to the point that important progress was made in the manufacture of sulphuric acid when the *periodical* combustion of sulphur *within* the acid-chambers was replaced by *continuous* work in *special apparatus attached to the chambers.* This led to making the sulphur-burners altogether independent of the chambers, and conveying the gas generated in the former by a flue into the latter.

Whilst in the old periodical style of working only the oxygen actually present in the chamber could come into play, and therefore after every combustion the chamber had to be supplied with fresh air by opening the door and a special valve, of course at the expense of much inconvenience and loss of gas, in the continuous style of work the necessary air constantly enters the burner by suitable openings at the same rate as the products of combustion are aspirated into the chamber by the draught prevailing throughout the apparatus. The continuity of work must be further aided by employing a combination of several burners, so that there shall always be burning sulphur present. There are also burners to which the brimstone is continuously supplied, in order to avoid the drawback of irregular supply of air and gas occurring even with the combination of several ordinary burners.

The plainest sulphur-burners, such as were the most usual in England, are represented in figs. 12 to 14.

The burner consists of a brick chamber covered by an arch, whose bottom is formed by a cast-iron plate, *a*, separately shown in fig. 14. This plate at the two long sides and one of the ends has a somewhat slanting-up flange of 3 inches height—in front, however, only 1 inch, so as to get out the ashes more easily. It

Fig. 12.

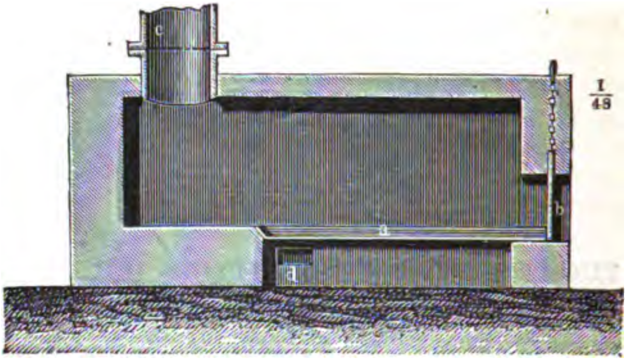


Fig. 13.

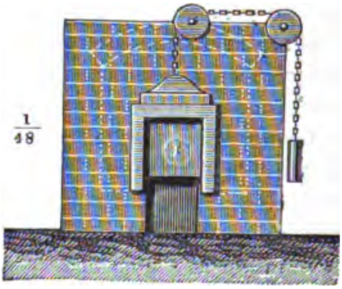
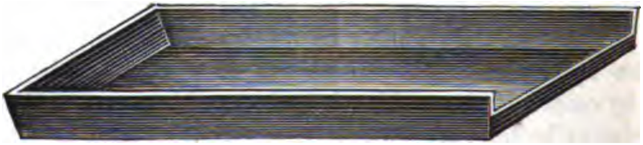


Fig. 14.



does not go right through the burner, but leaves the last third of it free, in order to give an opportunity to the sulphur vapour, which is always formed, of mixing with the excess of air and burning; rarely, however, this is completely performed, so as to entirely do away with any sublimation of sulphur. This not only causes a loss of sulphur, but also easily leads to the chamber-acid getting muddy and being covered by a thin membrane which prevents the contact between the bottom acid and the gas, very necessary for the chamber process. The burner is further provided with an iron door, *b*, sliding in a frame and adjustable by a chain and balance-weight; also with a pipe, *c*, for taking away the gas. An air-channel, *d*, below the plate is in connexion with a small chimney, or sometimes only with the open air, in order to cool the metal plate to some extent and prevent the sublimation of sulphur. There are always several furnaces of this kind combined together; each of them, with plates of 8 feet × 4 feet, can burn 5 cwt. of brimstone in 24 hours, which is put in in 6 portions, one every 4 hours; if four furnaces are combined, one of them is charged every hour. In these burners usually at the same time the nitric acid is liberated by placing cast-iron pots, provided with 3 feet and containing a mixture of nitre and vitriol, amidst the burning sulphur by means of large tongs.

For a start the plates are heated by a small fire of wood shavings, the door being left open, not till the iron becomes red hot, but only till the first charge of sulphur ignites of its own accord or can be easily lighted by a red-hot iron; the further charges always find the burner sufficiently warm. A special fire-grate below the plate, to be used only at the start, is quite unnecessary. The admission of air is regulated by opening the door, *b*, more or less widely; and its position is fixed by putting a wedge underneath the door, or by hooking the balance-chain to a nail driven into the brickwork outside. In the beginning, when the chambers are filled with air, the damper in the draught-tube is only opened gradually, to chase the air away more thoroughly.

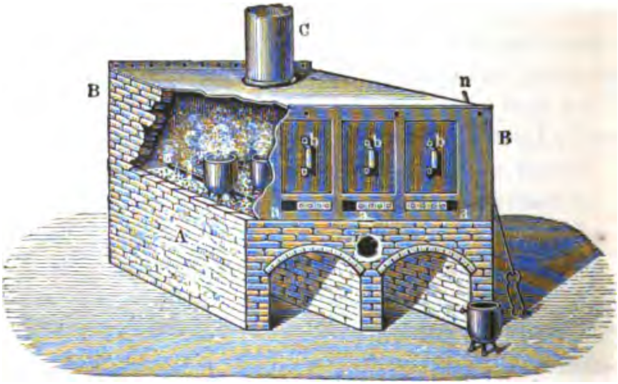
The style of working is generally rather rough; it must be considered that such burners are now-a-days hardly found in large works, where more supervision can take place. Before the attendant pulls up the door, he convinces himself of the state of the chambers so as to judge how much nitre he is to "pot" along with the brimstone. Often the nitre is merely measured by guesswork. First the brimstone is thrown in; the door is immediately let down, then a sufficient quantity of chamber-acid is poured into the nitre-pots, always by guesswork; the door is opened again, and the pots are placed among the brimstone, now already on fire, by means of an iron fork made for the purpose. The heat produced by the progress of the combustion drives off the nitric acid, and this enters the chambers along with the sulphurous acid.

When the time is up, the door is raised again, and the ashes are raked out; first, however, the nitre-pots are lifted out and emptied of their liquid contents. Then a new charge is made as above, and so forth. In all other sulphur-burners, excepting the continuous ones, the work is carried on in the same way; only the introduction of the nitre sometimes takes place in a less rough way, or nitric acid is used directly in the chambers.

It is a sign that the burner is working well if the brimstone burns with a pure blue flame; as soon as the flame takes a brown tinge, it is a sign that much sulphur is subliming, and care must then be taken to cool the plate by the flue underneath.

A somewhat more perfect apparatus is shown in fig. 15. A is the foundation, B the chamber for burning the sulphur, C the gas-pipe. The foundation carries a cast-iron plate which covers the whole furnace-bottom, and is inclined a little forward. The combustion-chambers are at the sides bounded by brick walls, but in front, at the back, and at the top by cast-iron plates; in front also are the charging-doors, *b b*, and small openings, *a a*, provided with slides for regulating the access of air. The furnace-bottom is divided by 3- or 4-inch iron bars into three compartments, corresponding to the doors and draught-holes, which are served by turns. Inside the pots are visible, into which the mixture of nitre and vitriol is charged. The details of construction are often very different from those shown in the diagram; there are burners with more or fewer working compartments, with different regulation of air, with rails over the bottom plates for pushing in a box instead of the nitre-pots, &c. The nitre-pots must receive a very small

Fig. 15.

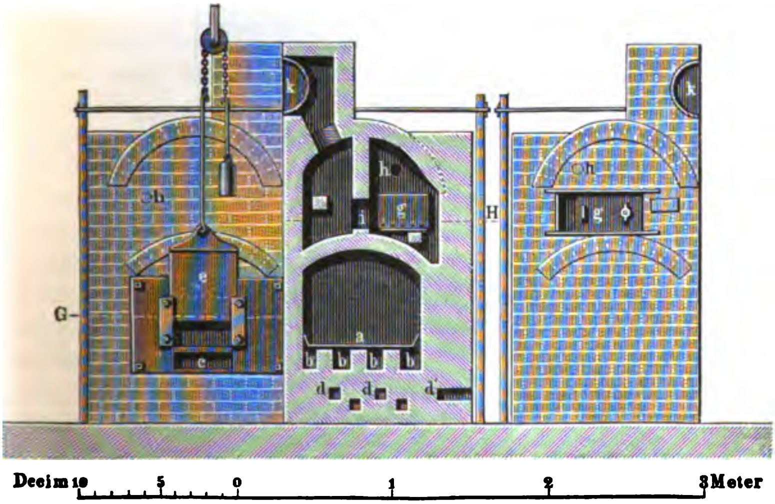


charge; otherwise the danger of boiling over is considerable, and the sodium sulphate among the brimstone is very troublesome. When nitric acid is used, the nitre-pots are not wanted at all.

Sometimes the iron sides of the sulphur-burners have been made double, and an air-channel has been left in the space between; thus, of course, the temperature of the burner could be regulated to a nicety by opening up a draught through the double iron wall when the burner got too hot, and shutting up the draught when it got too cold; but such iron burners are very soon worn out, and they have therefore frequently been given up again.

The diagrams figs. 16 to 19 show a set of two burners free from most of the drawbacks mentioned. Fig. 19 is a sectional plan taken at two different levels; fig. 18 a longitudinal section; fig. 16 half front elevation, half cross section; fig. 17 back elevation.

Fig. 16. Fig. 17.



a is the cast-iron bottom plate for burning the sulphur; it is carried hollow on pillars; and the channels *b b* formed thereby underneath the plate communicate with the outer air by the opening *c*, so that the plate can be cooled from below. The channels, *d d*, left in the foundation a little further below, communicate with this system, and ultimately end outside at *d'*. Owing to the difference of level and temperature, the air must always enter at *d'* and get out at *c*; its quantity can be easily regulated by partially closing *c*. The door, *e*, is hung in the usual way. The gas of the burner does not go straight to the chamber, but first ascends through the opening *f* into a space separated from the burner

Fig. 18.

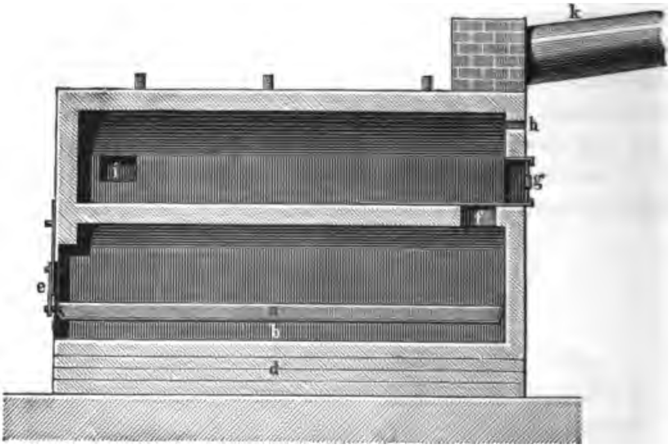
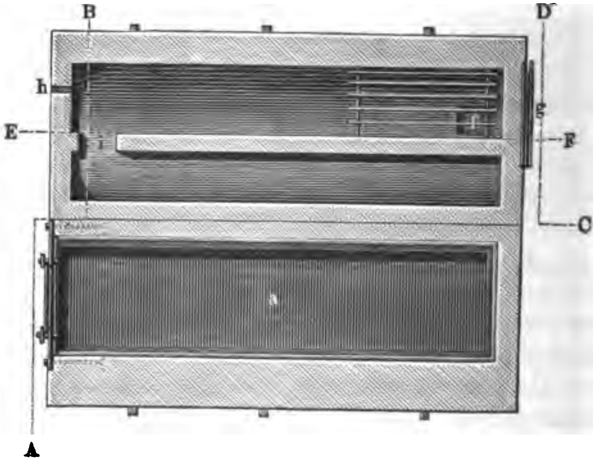


Fig. 19.

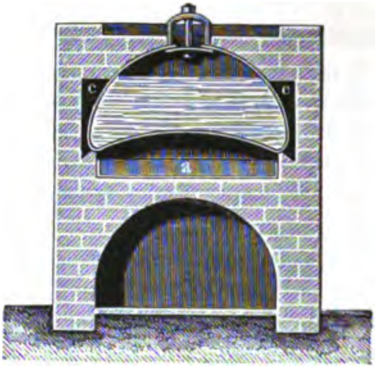


proper by an arch. Just above the opening there is a grating, on which the nitre-pots are put, being introduced by the door *g*. There is here a small hole, *h*, lined with an iron tube, for admitting a little more air to the upper compartment and burning any sublimed sulphur. The gas first returns to the front, then back again through the hole *i* and the second half of the upper compartment, and at last escapes through the cast-iron pipe *k*, common to two burners, whose upper stories are accordingly not built identically, but symmetrically.

This burner (known to the author from actual use) admits of very good regulation; the sublimed sulphur on its long way through the upper story is either deposited as such or burnt, and cannot get into the chambers. The boiling-over of the nitre-pots can here be made harmless by simple contrivances. This burner is in some points analogous to that of Harrison Blair (see below), but it is much simpler and adapted for a smaller scale of work. As a rule the working doors used to be closed within a very small fraction, and the admission of air to the upper story regulated by more or less closing the hole *b*. Four such furnaces worked together; every half-hour one of them was charged with ½ cwt. of brimstone.

In order to avoid the drawback common to all sulphur-burners, viz. the high temperature causing a sublimation of sulphur (which some have tried to avoid by wetting the brimstone with water), and in order even to turn it to use, the cover of the sulphur-burner is sometimes employed for drying wet materials; sometimes it has been made in the shape of a pan for heating water. In a few places a further step has been taken by giving to the burner a cover consisting of a peculiarly shaped cast-iron steam-boiler, as shown in fig. 20. The vapours of SO_2 generated in the plate *a* first heat the bottom of the boiler and then circulate round its sides by the flues *c c*; at last they go into the pipe leading to the chambers. In this way a good deal of fuel is said to have been saved; and the boilers are said to have suffered so little that at Kuhlmann's works they only required turning their back end foremost after the lapse of seven years. This is not in opposition to the above-mentioned fact that the iron walls of the furnace do not stand well, because the steam-boiler could neither be overheated nor was it in contact with the outer air. In spite of this the above arrangement has

Fig. 20.



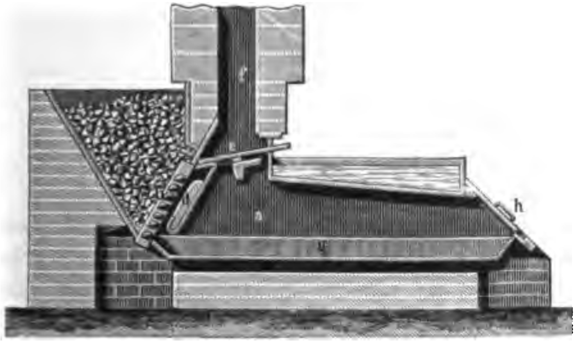
been given up again everywhere, probably because the generation of steam was too slow, and could not be depended upon for that regularity which is of paramount necessity in the manufacture of sulphuric acid.

Another arrangement, made by Kuhlmann later on, is said to have been more effective. He built for each set of chambers a furnace with four cast-iron ⌓-shaped retorts of the same kind as is usual in gas works. The retorts have at the front end openings for charging the sulphur and for the draught, at the back end pipes for taking away the gas. The brimstone burns on the flat bottom; the gases are carried away from the back end by long pipes to a wide common antechamber. On this long journey and in the chamber, where it travels slowly, the gas has sufficient time for cooling and for allowing the sublimed sulphur to subside.

All the sulphur-burners hitherto described are built on the intermittent plan; and unless a number of them were working together, they would yield a very unequal current of gas. As the brimstone, of course, must be allowed to burn off as completely as possible, the furnace in the later stage, and especially just before being recharged, yields very little sulphurous acid, whilst it is not possible to regulate the draught so that exactly so much less air is introduced as less sulphur is burnt. When at last the door is opened for a new charge, a very large amount of air rushes into the burner and further on to the chambers, without any sulphurous acid whatsoever. This irregularity, very prejudicial to the chamber process, is certainly to a great extent neutralized by the fact that always several furnaces (three, four, five, or more) work together in such a way that they are charged by turns; for instance, with a four hours' shift and four furnaces one furnace is charged each hour, and thus gives out least gas when its neighbours are fully burning. It has, however, been several times attempted to construct really *continuous burners*, which would save much labour, and, moreover, give a much better-regulated current of gas than can be given with single burners.

Petrie's burner, patented Nov. 1st, 1852, is intended to permit a totally equal combustion of the sulphur independently of the draught, to facilitate the removal of the ashes, and to avoid the escape of sulphurous acid or else the entrance of an excess of air during the charge of fresh brimstone. The furnace, *a* (fig. 21), is open at the back end, but provided with an inclined grating, *b*, whose horizontal bars do not allow any solid pieces of brimstone to fall through, whilst the melted sulphur can run through. The brimstone lies behind the grating; in front of it there is a screen, *d*, for protecting it from being overheated; the slide, *e*, serves for regulating the running-off of the melted sulphur, and for uninterruptedly admitting just as much as is wanted for producing sulphurous acid. The burning takes place on a plate, *g*, inclined a little towards the door, *h*; the latter serves for occasionally removing the ashes, and at the same time contains an adjustable opening for

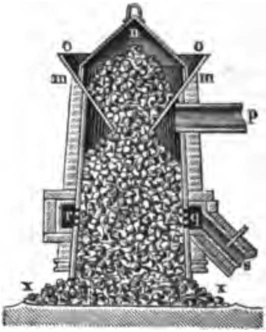
Fig. 21.



admitting air into the burner. An air-channel below the pan *g* acts in this way, that the air entering at one end *cools* it at the end where the combustion principally takes place, and then, as heated air, *warms* the lower end of the pan, next to the door, which contributes to fully burning the sulphur flowing that way. This furnace has not been successful, as the feeding with melted sulphur is not very regular, the sulphur easily gets into a tough state by overheating and does not at all run then, and the door *h* must be opened after all for the removal of the sulphur.

Petrie had also constructed another furnace (fig. 22) for burning the sulphur in the earthy residues or in similar mixtures. It consists of a cast-iron shaft and a brick jacket. The mass is introduced by the funnel *m*, whose cover *n* has a sand-lute, *o*; the formed sulphurous acid goes away by *p*. The previously heated air arrives through *s*, travels round the furnace in the channel *r*, and then enters into the furnace through the holes *q*. The whole furnace is open at the bottom and stands on feet, so that the burnt-off mass forms the heap *x x*, which is removed from time to time; here further air enters the furnace.

Fig. 22.



The object pursued by Petrie is attained in a more perfect way by the furnace of *Harrison Blair*, in which the volatilization of the sulphur, which otherwise is a source of inconvenience, is made use of for making the burning continuous. The apparatus consists of three parts, one of which serves for partly burning the sulphur and entirely volatilizing the unburnt portion; the second serves for completely burning the latter portion, the third for decomposing the nitre. Although both the former compartments are at a full red heat during the process, sublimation of sulphur is as good as impossible; and the process is as nearly continuous as possible, since the residue need only be withdrawn once in 24 hours. Fig. 23 shows a plan, fig. 24 a sectional elevation, of this burner.

Fig. 23.

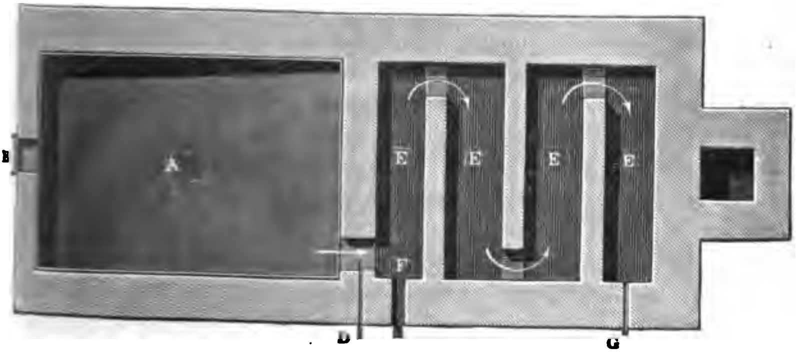
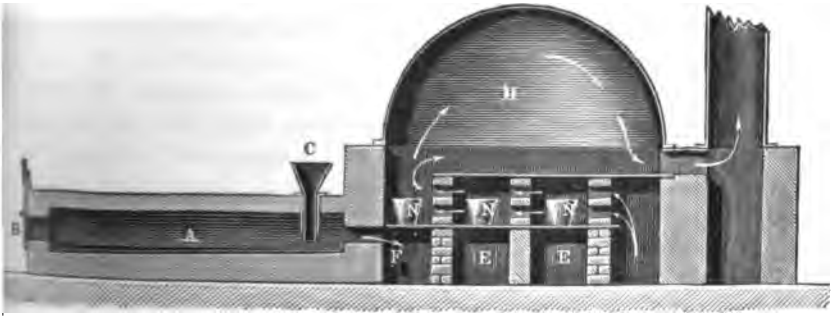


Fig. 24.



A is the space corresponding to an ordinary burner-plate, which has rather high sides and a descent towards the door; but 2 feet from the door it rises again a little, so that the residue raked to that part can burn out completely before it is removed by the door B, which takes place once in 24 hours. When this has been done, the residue raked together from the other parts of the burner is brought to the same place and allowed to burn for 24 hours again. The bottom of the burner is not made of iron, but of closely-set bricks with well-grouted joints. This space A is 9 feet long, 6 feet wide, and 1 foot high. The door B is an iron plate, loosely sliding in a frame, but a little slanting so that it closes almost air-tight, and is easily removed. It is perforated by a number of holes, which can be either partly or entirely closed by a slide. The brimstone is either put in once for 24 hours through the working-door, or gradually through a funnel C; C is continued by a 7-inch cast-iron pipe to within 6 inches from the bottom of the chamber; it is surrounded by a wider pipe to protect it against being burnt too quickly. The funnel and its continuation are always filled with brimstone; and this is always replaced again as it melts off at the bottom. The simpler kind of charging once every 24 hours through the door seems after all to have succeeded better. The admission of air through B is regulated so that only sufficient sulphur is burnt for keeping up the heat of the furnace; the largest part is simply evaporated. At the same time the regulation of the access of air allows of spreading the process evenly over the whole day. The walls of the furnace are made 1½ brick strong, in order to keep the heat together. The mixed gas and vapour enters through an opening of 9 × 9 inches (which can be closed by a fire-clay damper D) into the combustion-space proper, E E, 8 × 6 feet, divided by three partitions into four compartments, communicating alternately in front and back by openings 9 inches square. Here at the same time fresh air enters by the opening F, which is provided with a damper of 3 × 8 inches. Now sufficient air is admitted for burning all the sulphur, which can be recognized with certainty by the fact that on opening the plug G the entering air does not produce a new flame. The roof of the combustion-space, E, is formed by fire-tiles, above which a second story, the nitre-oven, is situated. There are three rows of nitre-pots, N, separated by reticulated brickwork, which also serves to support another roof of fire-tiles for covering the nitre-oven, altogether 18 inches high. The diagram shows how the hot gas must circulate round the nitre-pots. The pots are renewed every six hours, so that every two hours another row of pots has its turn. The hot gas, mixed with the nitre-gas, first passes underneath the cast-iron dome, H, for a partial cooling, then through an iron pipe, I, 24 feet high, into a small cooling-chamber of 18 feet length, 5 feet width, and 1½ foot height (whose bottom and top are covered with water), and then into the lead chambers. Later on, steam has been admitted into the combustion-furnace, which is said to hasten the formation of sulphuric acid. With a furnace of the dimensions stated, 26 tons of brimstone per week are said to have been burnt in a perfectly satisfactory way, corresponding to the work of 15 ordinary burners; by cutting off part of the air it was possible to reduce the sulphur burnt to 5 or 6 tons per week. For an equal chamber-space much more sulphur can be burnt than with ordinary burners without any damage to the process, owing to the even work and the avoiding of any excess of air. Indeed Blair's burner is much commended, and probably would have been employed much more largely, but that soon after its invention most large works (and only such can do with it) have passed over from brimstone to pyrites.

The following analysis of the residue from the sulphur-burners has been made by Richardson (Richardson and Watts, 'Chemical Technology,' vol. i. pt. v. p. 198):—

Sodium sulphate*	13·77
Calcium sulphate†	28·49
Calcium silicate†	15·91
Sodium silicate	1·10
Ferric oxide and alumina	2·80
Water and sulphuric acid*	13·05
Insoluble	24·29
	99·41

A special *cooling of the gas* from sulphur-burners is, as a rule, not only unnecessary, but even injurious; so that, for instance, in the furnace shown in fig. 18 the vertical metal pipe conveying the gas to the chamber had to be protected against cooling by a brick jacket. Even where no cooling takes place by water-pans, steam-boilers, &c., the gas gets into the draught-pipe at only about 100° or 120° C. temperature, which is just sufficient not to allow the nitric acid to condense before it gets into the chambers, a contingency decidedly to be avoided. Where water-tanks, steam-boilers, &c. are used, the temperature of the gas is said to come down as low as 40° C.; in this case only liquid nitric acid can be used for the chambers. In Blair's continuous burner the temperature certainly rises much higher; and in this case a cooling-arrangement, such as that described, must be resorted to.

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* The sodium sulphate and the free sulphuric acid (or rather the acid sulphate) evidently come from the nitre-pots boiling over.

† The lime no doubt partly comes from the brickwork of the furnace.

CHAPTER VI.

THE PRODUCTION OF SULPHUROUS ACID FROM PYRITES.

The pyrites, as it comes into the market, is always sufficiently pure to make a separation from gangue unnecessary. This is only required for pyrites picked from coals ("coal-brasses"); but this does not exactly concern us here, as it is only a locally-used by-product.

It is, however, always necessary to break up the larger lumps in order to burn the pyrites completely; and this is always done at the works themselves—except in a few cases, where they buy smalls direct from the mines. The majority of the factories break the ore by hand; and it is found that different descriptions of ore behave very differently in that respect. The Norwegian ore is the hardest; here the large lumps have to be broken with great labour by means of 20-lb. fore-hammers. The Westphalian ore is much more easily broken—still more easily the Spanish and Portuguese and some of the French ores; these, however, make a good deal more smalls, 10 per cent. and more. The softest ore is that of Chessy, consisting of loosely aggregated individual crystals, which by a blow of the hammer fall to powder. Some of the Spanish ores are equally roughly crystallized; these ores are very troublesome for use as lumps.

In England the ore is generally broken so that all the pieces pass through a sieve with 3-inch holes. At Oker only pieces of 1¼ inch side are allowed for ordinary burners, and of 2½ inches for deep kilns. On the other hand, as few smalls as possible are made. The broken ore must be sifted again to separate the smalls, for which purpose some works pass it through a half-inch, others through a quarter-inch riddle. What remains on the riddle is *lumps*; what passes through, *smalls* or *dust*. Both of them have to be treated separately. It is very important that the ore be used neither in too large nor in too small pieces. In the former case it does not burn right through; there remain green cores in the interior of the cinders, which can be seen on breaking them up. These large lumps also get too hot on burning, and may cause the formation of slags (scars) by production of FeS, as will be explained hereafter. If, on the other hand, the pieces are too small, they too much prevent the access of air, and similar results follow from it as in the former case.

Sometimes three sizes are made—lumps, peas, and dust,—but mostly only where there is a special burner for the "peas."

Owing to the great manual labour required for the breaking of pyrites, the same mechanical stone-breakers have been introduced for this purpose which originally were made for road-metal. The best of these machines is that of Blake, built by Messrs. Marsden of Leeds, which is shown in figs. 25 & 26. This machine is made of various sizes, and accordingly varies in the amount of work turned out and in the size of stones it can attack. A and B are the two active parts, the "jaws." A is fast and perpendicular, B movable, and makes with A an angle of 72°, by oscillating a little round the fixed shaft, D. This movement is communicated to the jaw B from the main shaft, H, by means of the angle-lever, E E′, and the crank motion, G H, so that the angle-lever presses the jaw B against the stones charged, the return motion of B being caused by a spring, F, cased in india-rubber. The angle-lever is adjustable by the wedge, N, lying behind its arm E′. The roller, C, causes a regular throwing-out of the broken stones; it receives its motion by a belt from the main shaft, by means of the pulleys, K, L, and the expanding roller, M. The crank-shaft, H, is also driven by a belt from the fast and loose pulleys, I I′. The machine is mounted on a four-wheeled bogie. It makes a great deal of noise, and needs frequent repairs; but the jaws, which principally suffer, are so arranged as to be easily replaced.

Blake's engine has been improved by Broadbent & Son, of Staleybridge, who have replaced the spring bedded in india-rubber by a simple, easily-adjustable lever arrangement, which saves labour as compared with the original arrangement. Output, according to size, from 40 to 130 tons in ten hours; price £140 to £375.

At Oker, a steam-engine of 12 horse-power drives two stonebreakers, mounted one above the other. The higher one breaks the large stones roughly, the lower one down to the proper size.

Fig. 25.

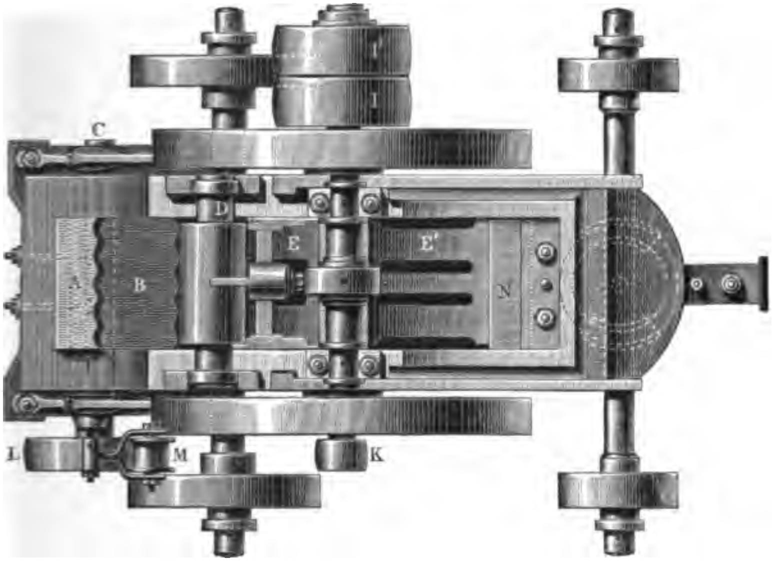
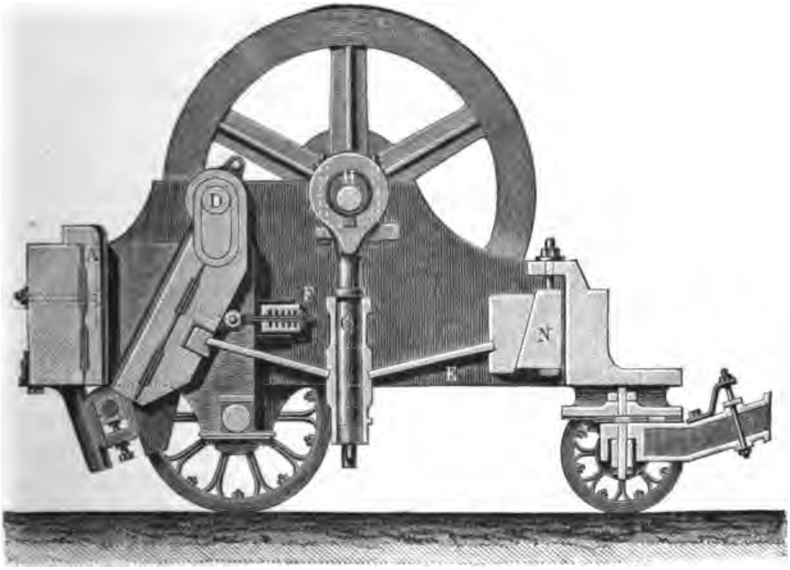


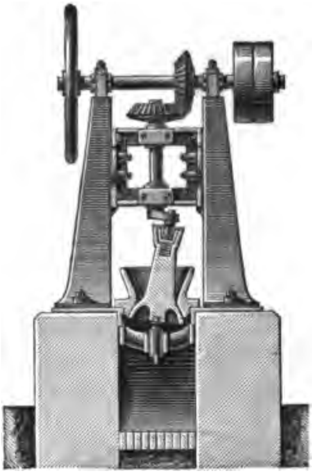
Fig. 26.



They supply, in the case of very hard ore, and a size of 1¼ inch, 25 tons daily; at 2½ inches size, 40 tons.

A new crushing-mill has been invented by Motte at Dampreny, near Charleroi, which has been improved by the Markish Engine Works (German Patent, October 16th, 1877; 'Dingler's Journal,' ccxxvii. p. 58). The principle is that of a peculiar kind of mortar, with hollow bottom, in which the crushing is done by a pestle, as seen in fig. 27. Whether this mill is really preferable to the older stone-breaking machines experience will show.

Fig. 27.

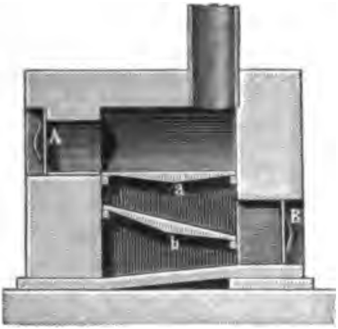


Pyrites-Burners.

Among the apparatus for burning pyrites in the manufacture of sulphuric acid a distinction has to be made between those intended for lumps and those intended for smalls. It is indispensable to keep both kinds apart, and to employ different apparatus, or at least processes, for them; for if the broken ore is put into the burner without separating the smalls, the air-channels, which ought to remain between the pieces, are soon partly stopped up with powder, and the access of air becomes irregular; thus scars are formed, and proper work is then impossible. Apart from the coarser and finer powder obtained on breaking, a great deal of smalls comes into the trade direct from the mines, obtained there by the use of water for separating the ore from the gangue.

We shall first describe the *burning of pyrites in lumps.* This always takes place in such a way that the heat of the burning pyrites suffices for maintaining the combustion without any other fuel being employed. The apparatus used for this purpose are called "kilns," or "burners." The first burner in which Farmer employed pyrites was a small furnace with two grates, fig. 28. A was the working-door, *a* the proper grate, shaped like an ordinary coal-grate, *b* a small grate for burning that which fell through the first, B the door for removing the cinders. Such a grate could not answer for pyrites; and therefore a step backwards was taken by employing real kilns without a grate.

Fig. 28.



Figs. 29 to 31 show such a kiln on a scale of $\frac{1}{10}$ of the real size, of 10 feet height, and 3 feet 3 inches width. Fig. 29 is partly a front elevation, partly a section through the line C D of the plan, fig. 30; fig. 31 a section through the line E F of the plan, showing the slope of the bottom to both sides, to facilitate the sliding-off of the cinders from the edge *c* towards the drawing-out holes, *b b'*. The ore is charged from the top through an opening, closed by an iron door. The air enters partly through *b* and *b'*, partly through four openings, *d*, higher up, which are partially closed by loose bricks according to requirement. These openings also serve for breaking up the burning pyrites by means of pokers. This is especially needed for cupreous pyrites, which is more easily fusible. The height of the charge in the kiln is variable, according to the nature of the materials; less-easily-burning ore must be kept at a greater

Fig. 30.

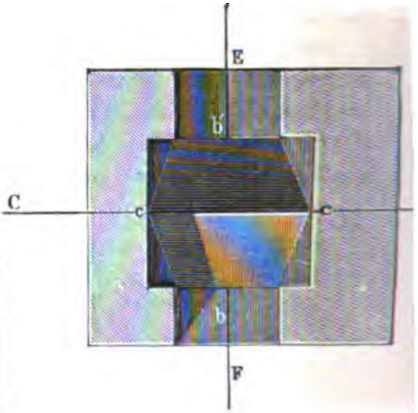


Fig. 29

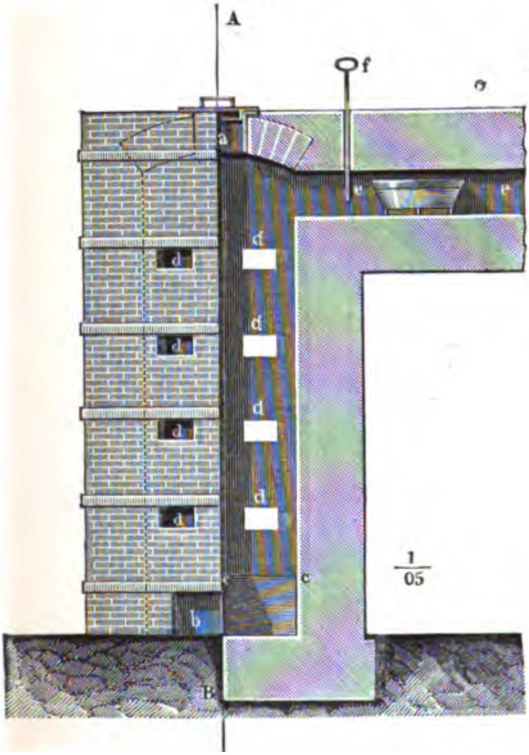
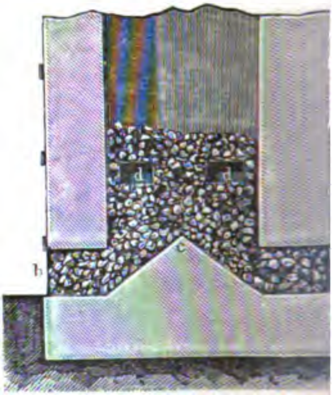


Fig. 31.



height. Special care has to be taken that no sulphur can sublime, but that the upper parts of the ore receive sufficient air for burning any sulphur that may have been volatilized. The gas goes through *e* into the acid-chambers, frequently, however, first through a brick chamber for depositing the dust carried away. If the nitric acid is to be generated from solid nitrate, the "potting" is done through a well-closing door in the flue, *e*, the temperature of which is high enough for the purpose. Six kilns are generally built together, each three of them with a common flue, *e e*, for potting, and a slide, *f*, for regulating the draught. The two flues, *e e*, are joined in a common flue, 3 feet 3 inches wide. According to Knapp ('Chemische Technologie,' vol. i. pt. 2, p. 306), the ore can be easily burnt down to 3 per cent. sulphur in those kilns; but this appears doubtful, as such a result is considered excellent even with the modern burners supplied with grates. Similar furnaces, with a saddle-shaped bottom, are still in use at Oker for ores poor in sulphur, whilst the rich ores are burnt in burners supplied with grates.

The square section, as shown in figs. 29 to 31, is mostly unsuitable for such high kilns, because the ore easily gets fast, and cannot go down, and also prevents the air from passing through. Therefore the kilns have more frequently been built with walls tapering a little downwards, such as are shown in most of the following figures. The sloping sides assist the sliding-down of the ore; and the greater surface causes the combustion to take place to a smaller extent in the interior of the mass, whereby its fusion is more easily avoided. Such a shape is that of the Oker kilns for burning the Rammelsberg ores (figs. 32 to 35).

Fig. 32.

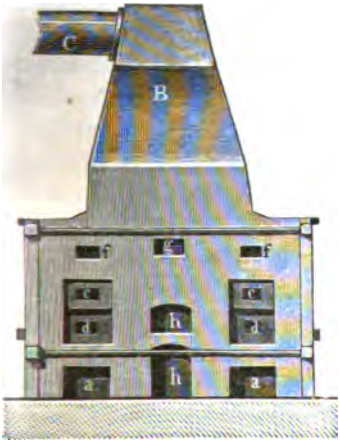
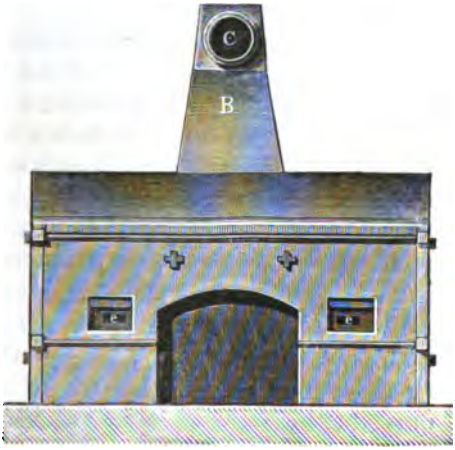


Fig. 33.



Four or eight kilns are built together. A A are the burning-shafts, 6 feet 6½ inches high, 2 feet 1 inch square at the bottom, 4 feet 2 inches square at the top; B, the gas-flues, joining in C′.

Each shaft has four openings in front, one on each side, two inwards; *ff* serve for charging the ore, *a a b b* for discharging the burnt ore and introducing air, *c e d i* for breaking up the pyrites or introducing more ore. The arch below the pillar, D, on which the potting takes place through *g*, is accessible through *h h*. Each kiln is broken up and charged every eight hours.

Fig. 34.

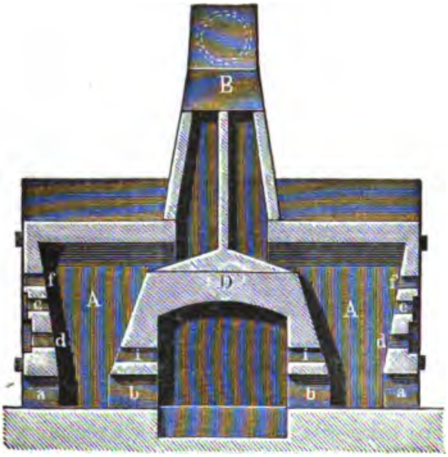
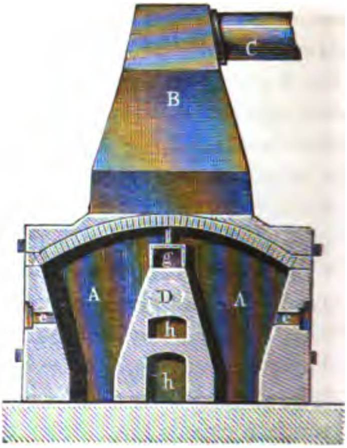


Fig. 35.



At Freiberg the drawbacks of the kilns with straight walls have been overcome by a shaft of oblong section, whose inside measurements are 8 feet 2½ inches height, 8 feet 2½ inches × 3 feet 7 inches width at the top, 6 feet 6½ inches × 1 foot 8 inches width at the bottom. This shape is said to answer best for poor, badly-burning ores. Altogether, the kilns hitherto discussed mostly serve for metallurgical purposes, such as roasting of coarse metal in copper and lead-smelting, for copper-pyrites &c., where only a portion of the sulphur is sought to be utilized; also for poor ores in general, where the needful temperature cannot be attained in burners with grates, and where a fusing of the ores does not take place in spite of the greater height of the kilns. Owing to this height, the ores must be employed in sizes at least upwards of that of a walnut; for smaller sizes, at Oker, burners with grates must be employed (Bräuning).

The Chessy kiln, figured in Payen's 'Précis de Chimie industrielle,' also belongs to the class of kilns without grates, but has long been replaced by more suitable apparatus. Perret, indeed, had employed an ordinary lime-kiln for his first experiments.

Latterly the pyrites-burners, apart from the just-mentioned metallurgical objects, have been generally constructed with grates and ash-pits. This certainly causes a considerable improvement in the working of the furnaces. Where the air has merely to pass through a mass of burnt ore, its quantity cannot possibly be regulated in this way, but only by dampers at the other end of the furnace. It is even a more serious disadvantage that the subdivision of the air inside the burner must be very irregular in that case. According to the greater or smaller resistance offered by the individual portions of the layer of pyrites, the air will pass through very unequally, and just in the least degree at the places where most pyrites is lying and where it is most wanted. The addition of a grate and a closed ash-pit alters the state of the case at once, in this way, that only a definite quantity of air need be admitted into the ash-pit, and that, moreover, this air must first spread equally underneath the grate, and rise all over the area of the burner. Thus the ore is much more completely burnt, and at the same time richer gas is obtained, which leads to a better chamber-process, higher yield of acid, and smaller consumption of nitre; the operation of drawing out the burnt ore becomes much more regular, and offers a greater guarantee against raw ore getting into it; lastly, it does not happen so often that fused masses, "scars," are formed in the burner, although also in the case of grates this easily happens if the style of working is faulty.

The introduction of grates led to further improvements:—first, a diminution of the height of the burners, which made them much handier for working, and which acted especially well with more easily fusible ores, although in some places the other extreme of too low layers of pyrites has been resorted to. Also the way of introducing the nitre has been very much improved; but in many cases this has been a sore point, even up to very recent times. The mixture of nitre and sulphuric acid is very apt to boil over; and the running over acid saltcake, if it gets into the burner, is not merely lost, but it disturbs the draught, and causes the ore to cake together in extremely hard masses, which can only be removed after pulling down the front wall. Other improvements will be mentioned later on.

A transition from the metallurgical kilns to the burners of to-day is presented by the Freiberg kilns for roasting 18 or 20 cwt. of coarse metal, with 20 or 21 per cent. of sulphur, in 24 hours (figs. 36 and 37). A is the shaft; *a*, charging-holes, 12½ inches wide, covered with iron plates, upon which a layer of coarse metal, 1 or 2 feet deep, is tipped; *b*, three larger working-holes, 15 inches long by 12 inches high; *c*, three rows of working-holes, 8 inches by 4 inches; *d*, three drawing-out holes on each side, 2 feet by 1 foot; *e*, saddle grates; F, air-flue; *g*, flue for taking away the sulphurous acid. The saddle grate is for the purpose of conveying air into the middle of the shaft, where it penetrates less easily than along the sides.

Fig. 36.

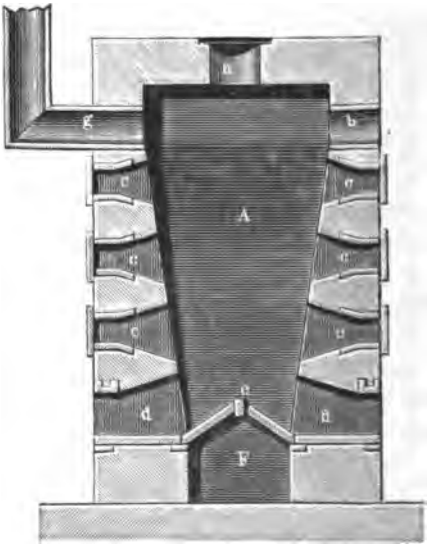
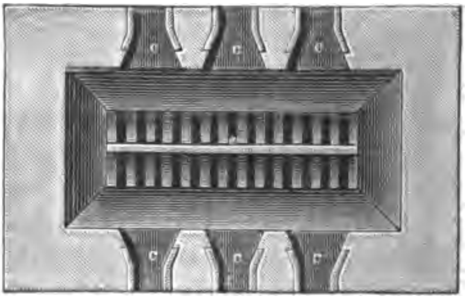


Fig. 37.



Before we enter upon the description of the burners, such as they are built now-a-days, we must shortly mention the *Belgian hearth-furnaces*, which possess grates, but which surpass the fault of too high shafts by the worse fault of too shallow and large hearths. These furnaces are described and figured in detail on pages 19 and 20 of an official report made (by Stas) to the Belgian Parliament on the 26th February, 1856 ("Fabriques de Produits Chimiques," Rapport par la Commission d'enquête &c.; abstracted in 'Dingler's Journal,' cxlv. pp. 375, 427). The furnaces had a grate-surface of 130 to 150, even 200 square feet. The grate-bars were distant 1¼ inch from each other, and were loose, but not movable round their axis. One third of them were put more closely together, for burning smaller ore. Three hoppers in the furnace-roof served for charging, lateral doors for working (and partly for charging), a cave, 6½ feet high and equally wide, for drawing the cinders. Each furnace received, in 24 hours, 2 to 3 tons of ore, in four or eight portions, partly pieces of 1½ to 1¼ inch side, partly cakes of pyrites dust, clay, and straw, of 4 inches diameter. The pyrites lay 8 to 12 inches deep. On drawing the cinders there was a great loss of sulphurous acid, because on opening the iron plate which closed the large cave a large quantity of air entered and drove out a great deal of sulphurous acid, as every practical man will readily see. The cinders must have contained much raw ore. The burning must have been very unequal in different parts of the grate and at different periods; and the evolution of gas must have been similarly unequal. It is no wonder that these works only yielded, on the average, 69 per cent. of the amount indicated by theory. The commission of inquiry recommended to employ smaller furnaces, to charge these by turns, in order to obtain a more regular composition of the gas, and to employ a deeper layer of pyrites, in order to increase the points of contact, and not to allow too great an excess of air to pass through. Chandelon reported in 1871 that most of these recommendations had been carried out, and that, indeed, the average yield had thereby been brought to 88·7 per cent. of the theoretical one ('Bulletin de la Société d'encouragement,' xviii. p. 315); but the author has seen burners with very shallow layers of pyrites even since then.

Less irrational than the former large Belgian furnaces, but still very faulty, are the *Marseilles burners* (figs. 38 and 39). Each of these burners, of which two or more are combined, contains two hearths, A and A′, for the roughly broken pyrites, and between them a basin, B, of cast iron, or acid-proof sandstone, for the nitre mixture. The gas escapes by the flues *o* and *d*; the wall *c* protects the basin, B, from being overheated. If the drawing (taken from Knapp's 'Chemische Technologie') is correct, the furnace on the left hand *must* have had too much, that on the right hand too little draught; and this will hardly have been overcome by regulating the slits in the doors. Both hearths together received 6 cwt. of ore every three or four hours—that is, 2 tons to 2 tons 8 cwt. in 24 hours. On drawing, apparently the whole mass of the ore was raked out. The lumps ought not to be too small; and 10 to 15 per cent. of sulphur is said to remain in the cinders. The layer of ore is much too shallow, and the whole construction objectionable.

Fig. 38.

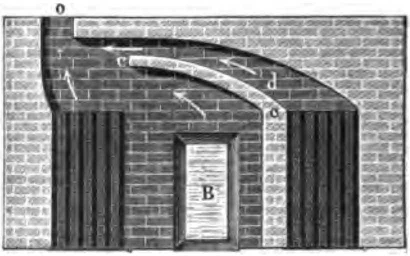
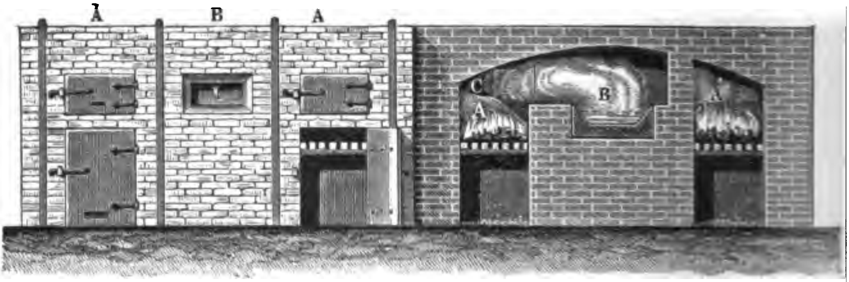


Fig. 39.



We approach the constructions of to-day with the Freiberg burner, shown in figs. 40 to 42. Fig. 40 gives an elevation through *c d* and *d e* of the plan, fig. 41, on a scale of 1 : 50; fig. 42, a sectional elevation through *a b* of the plan. This burner is specially adapted for easily-burning ore. B is the shaft; *f* the charging-hole, furnished with a tightly closing cover. The grate, *g*, still shaped like that of a steam-boiler, is inclined, in order to

Fig. 40.

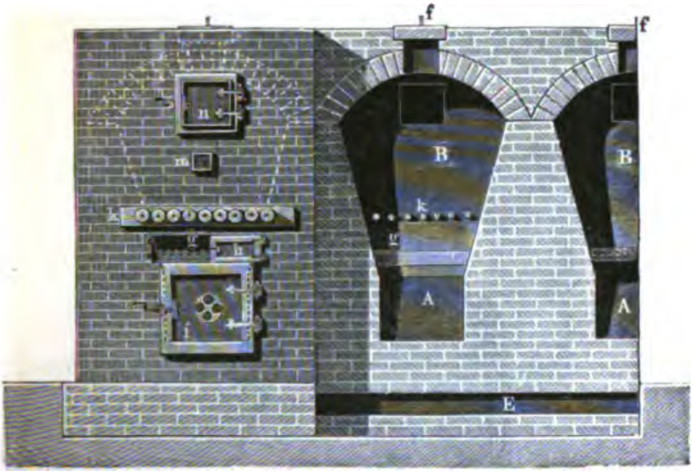
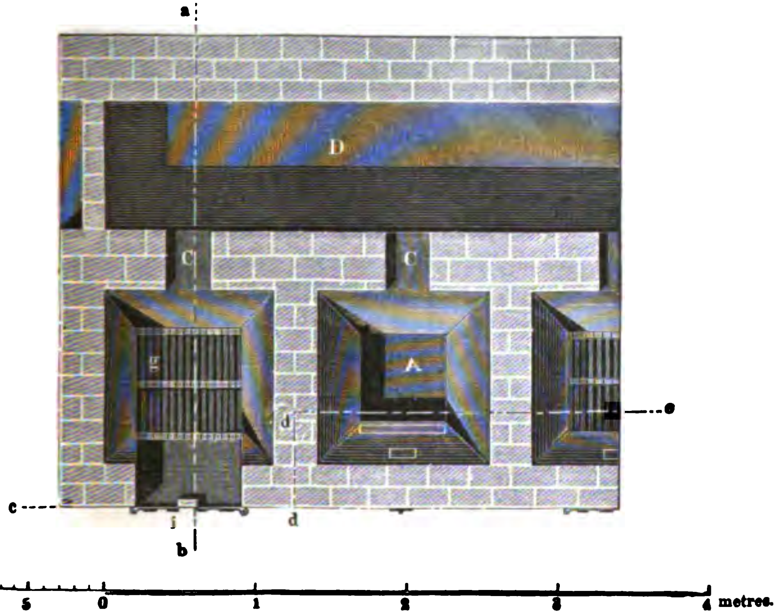
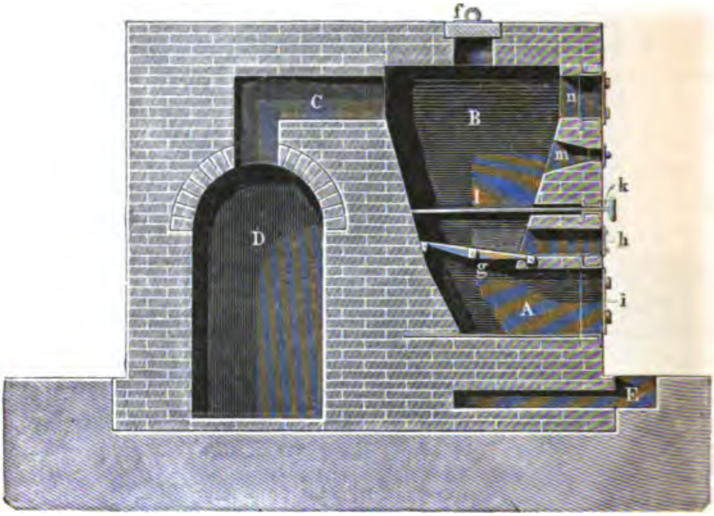


Fig. 41.



facilitate the drawing through *h*. The smaller pieces fall through the grate into the ash-pit, A, and are emptied from time to time through the door, *i*, furnished with holes for the supply of air.

Fig. 42.



About 10 inches above the grate the front wall of the burner is pierced by a horizontal row of holes, *k*, in which stuffing-boxes are fixed for movable round iron bars, *l*. These can be used for loosening the ore (which they will do very incompletely); they also serve for supporting the higher-lying portions of ore on withdrawing the cinders. The door, *m*, serves for observing the combustion (which, however, can only be judged of properly from the top) and for introducing a poker in case the ore must be broken up. The larger opening, *n*, likewise with a door, serves for the same purpose, and also for potting in the flue, C (which must be a very troublesome thing, looking at the large size of B, connected with great risk of spilling the contents of the nitre-pots). The gases from C get first into the large main flue, D, which at Freiberg is upwards of 330 feet long; here they deposit dust, and especially arsenic, and then pass on to the acid-chambers. The flue E serves for keeping the ground-moisture from the burners.

Whilst on the Continent there was still an oscillation between the extremes of high kilns and of hearth-furnaces, in England already, since about 1860 or 1862, an intermediate form had been found, which, in all essential parts, is the same as that used now, and is being more and more introduced on the Continent. The English pyrites-burners have a moderate area of grate, about 4 to 5 feet wide, and 4½ to 6 feet from front to back. The inner walls sometimes rise quite perpendicularly; more frequently the two sides and the back slant a little outwards, up to the level of the working-door, to the extent of about 9 inches, sometimes only 6 inches, in width, and half as much in the back; from that level the walls rise again perpendicularly up to the roof. The front wall, which is only 9 inches thick, and mostly protected by a 1-inch or 1½-inch metal plate, rises perpendicularly, and is perforated with several working-holes. The ash-pit has either vertical sides or, more rarely, sides converging towards the bottom, in order to facilitate the removal of the cinders. Its depth varies from 16 to 24 inches. The level of the working-doors, which determines the depth of the layer of pyrites, varies from 1 foot 8 inches to 2 feet 6 inches; but the former depth is considered by most practical men too little, at any rate for average ores, and the right depth is between 2 feet and 2 feet 4 inches, but nearer the upper than the lower limit. At the Oker works the depth of ore is only 1 foot 6½ inches, and elsewhere in Germany similarly, even down to 1 foot 4 inches. The reason of it is the fear of scarring, which English experience with the same ores proves to be unfounded. The height from the upper level of the ore up to the abutment of the arch is usually about equal to that of the working-door, say 9½ to 12 inches, and from there up to the crown of the arch another 8 or 9 inches. The arch itself is either sprung from side to side, as is the custom on the Tyne (whereby the walls are made to bear the weight more equally and the working through the doors is facilitated), or, as is usual in Lancashire, from front to back (which is more advisable in the case of two rows of burners being built back to back, in which case the arch is sprung over both burners together, with a supporting wall in the centre: comp. fig. 54). In any case it is advisable to build the burners back to back, even with arches sprung from side to side, wherever it is locally possible; thus one back wall is saved, the heat is kept up better, and a common gas-flue can be employed.

The *gas-flue* of the English burners is always at the top, each burner-arch having a hole of 4 to 5 inches square leading into it.

These holes are not always provided with dampers; but by gradually increasing the size of the whole as the distance from the main shaft becomes greater, evenness of draught is produced. The flue itself can be made of bricks set in tar and sand, and covered with fire-tiles. Most modern works prefer forming it by a second arch, about 6 or 12 inches above the burner-roof, reaching right across the whole burner, and supported by the front plate being made high enough. Special care is devoted to the *doors*, as will be seen when we give the detailed description.

The principal feature of the English pyrites-burners, which has now been introduced into nearly all continental works as well, is the employment of grate-bars of square or oblong section, movable in bearings, and leaving larger or smaller spaces between them, according to their position. (According to Hasenclever, in Hofmann's 'Bericht,' 1875, i. p. 158, movable grate-bars have been used in France ever since 1848.) Fig. 43 represents such a grate-bar, in which the places can be noticed which are forged or cast round, so that they can easily turn in the respective hollows of the bearers. Bars 2 inches square are usually made of wrought iron; the oblong bars, 2 by 3 inches, which, being turned on edge, leave a larger space, and therefore only suit larger pieces, are mostly of cast iron. The grates rest on cast-iron bearers, as shown in fig. 44; in the shallower kilns (4½ to 5 feet from front to back) there are two such, in the deeper kilns (5 feet 3 inches to 6 feet from front to back inside) three. According to this, of course, two or three rounded places must be made on the bars themselves. Lest these should be weakened too much, the diameter of the round places in the square bars is equal to the side of the square, in the oblong ones equal to the smaller side. In any case the front piece of each

Fig. 43.

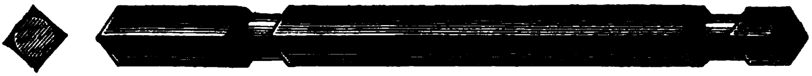
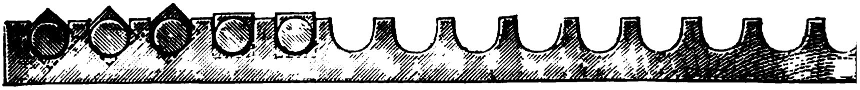


Fig. 44.



bar, where it projects beyond the bearing-bar, remains square or oblong, so that it can be turned round its axis by means of a suitable key (fig. 45). The intervals between the grate-bars are mostly managed so that with 2-inch bars they are about 2 inches when the bars are in the situation shown in fig. 46; but if they are turned 90 degrees, as in fig. 47, the intervals will only amount to 1¼ inch. In another actual instance the diameter of the bars was 1¼ inch, the clear distance in the straight position 1½ inch, in the diagonal position 1 inch. If, lastly, the situation is as in fig. 48, where half of the bars are turned, the intervals will be between the two above limits; and as each bar can be turned separately, many combinations can be produced. Usually the bars stand as in fig. 47—that is, all with their diagonals in a horizontal plane, or with the smallest possible intervals, so that the pieces of ore cannot fall through. As soon as a portion of the ore has to be removed, the attendant takes hold of the front end of a bar with his key, and

Fig. 45.

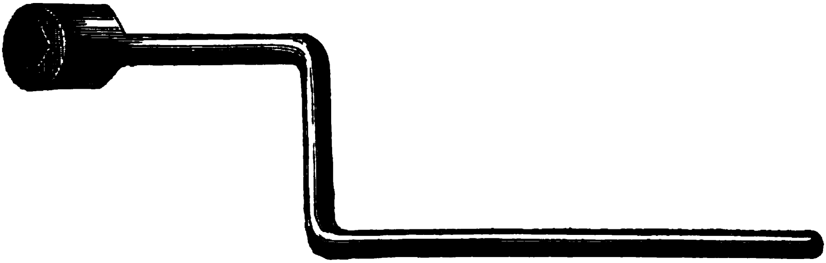


Fig. 46.

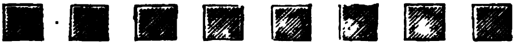


Fig. 47.

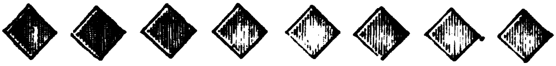
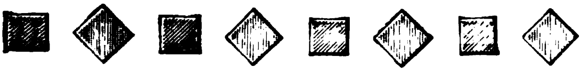
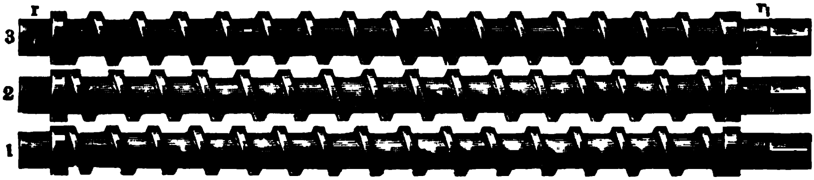


Fig. 48.



moves it a few times from side to side. Thus a kind of crushing-action will be exercised on the cinders getting between the two bars, the intervals are momentarily enlarged, and that which is jammed between the bars is forced downwards. Of course a good deal of strength is required for this work. At the same time, by the action of the key, the pyrites is loosened up to a certain height. The workman now goes from one bar to another, generally leaving one out, and shakes them, according to the judgment of the eye, so far that an equal quantity of burnt ore is drawn out all over the area of the grate. That which has fallen through is allowed to lie in the ash-pit till the time comes, once every 24 hours, for opening the bottom door and taking away the cinders. A new shape of bars, which is said to possess great advantages over the ordinary angular ones, has been patented by W. Helbig (Dingl. Journ. ccxxvii. p. 67), and is shown in fig. 49. It is that of a cast-iron bar, of round, square, or elliptic section, with a worm all round it. The pitch and cross section of the thread are made to suit the maximum and minimum size of the pyrites for which the grate is intended. The collars, *r* and r_1, protect the bar from getting out of its bearings; *c* is the back bearing, *f* the front bearing, with a square continuation for receiving the key. The diagram shows the different positions of the bars. When they stand as 1 to 2, they offer the smallest, when they stand as 2 to 3, the largest openings. In either case the total area of the openings is always the same, different from the ordinary burner-grates. Helbig claims the following advantages for his bars (which, however, are partly shared by the usual ones):—The bars, owing to their round shape, are more easily turned, without lifting or shaking up the pyrites; so that no incompletely burnt pyrites comes down too quickly. [This does not seem very advantageous; the shaking up of the ore is even useful in order

Fig. 49.



to prevent it from getting fast.] When larger pieces are jammed between the bars they can be broken up more forcibly. The ore is very evenly burnt, owing to its going down so evenly. On account of the peculiar front bearings, no air can enter there. No pyrites falls out without turning. The injurious effect of the pieces bursting is counteracted [in what way?]. That the grate-surface remains the same in each position of the bars is of great importance for the regularity of the burning. These grates are said to be as well adapted as Walter's burners for the burning of "peas" (see below).

It is very acceptable (but rarely met with, because it necessitates a somewhat complicated plant) if the ash-pit is deep enough for introducing an iron bogie below the grate whose top equals the whole surface of the grate in size; the ash-pit door, of course, must be correspondingly large. The cinders in that case fall direct into the bogie, and can be wheeled out in a few moments; usually they have to be raked out by hand, during which time the door must stand open, and much false air gets into the burner. This arrangement is found in Hasenclever and Helbig's burner, figs. 60 and 61, also at the Oker works. Where there are not two rows of burners built back to back, it is possible to charge on one side and discharge on the other; but there is no great advantage in this arrangement, which takes a great deal of space.

In the South of France at present similar burners are used, 5 feet 11 inches deep, with a grate-surface of 13 square feet, and a distance of 1½ inch between the bars when in a vertical position; in these, lumps, along with 10 or 15 per cent. of "balls," are burnt down to 2 or 3 per cent. of sulphur (Favre, 'Moniteur Scientif.' 1876, p. 270).

In order not to be obliged to open the whole ash-pit when shaking the bars, all better furnaces are provided with a slit in the front plate, through which the ends of the bars are accessible. Except during shaking-time, the slit is covered by a door, which is best made in two halves.

All doors for charging, working, shaking of the bars, and getting out the cinders either run horizontally in grooves, or, still better, they are hung on hinges; and the door-frame, cast upon the front plate, is made to slant forwards below, sometimes also sideways, so that the door lies fast upon it by its own weight. As both the door-frame and the edges of the door touching it are planed, the doors close tight without any luting, whilst those running in grooves must be made tight with lime-putty.

All brickwork, so far as it is touched by the heat (that is, the walls above the grates, the arch, and the gas-flue), are lined with fire-bricks; the total thickness in front is one brick, behind (or as the partition between two rows of burners) two bricks. The side walls dividing each two burners of a row are 1½ or 2 bricks thick, but they diminish upwards to one brick. The roof need only be 4½ inches thick. The mortar is fire-clay, as usual; in the colder parts, such as vertical gas-shafts, flues, &c., this does not stand so well as boiled-down tar and sand.

Of course the burners are well bound together, either by special uprights and tension-bars, or by flanges cast to the front plates, provided with holes for the cross bars (fig. 52).

Opinions as to what size the burners are to be made vary a good deal. Mostly smaller burners are met with, about 4 feet 6 inches to 5 feet from the outside to the inside of the back wall. The reason given for this is that longer grates cannot be served so well, and that in a larger burner the newly-charged ore forms too shallow a layer (the depth of the whole layer of pyrites, including the partially burnt ore, is not in question here). The author has, however, worked for a good many years with larger burners, nearly 6 feet from the front to the back end of the grate, and has burnt his ore better than the majority of other works using the smaller burners. To be sure, the usual 7-cwt. charge had to be all put in at once, whilst in the smaller burners it is put in in two halves every 12 hours; and many practical men assert that a 12-hours' is preferable to a 24-hours' charging; but this is not borne out by experience. It is, however, a decided mistake to try burning a much larger charge on the larger grate, say 8 or 9 cwt. This can only be done with poor ores, such as are not in use now-a-days, except locally; richer ores, especially those containing copper, are sure to be fluxed by the heat getting too high, and cause the greatest trouble. As a result of long experience, the author is inclined to consider a grate-surface of 4 feet 6 inches by 5 feet 8 inches, and a depth of pyrites of 2 feet 3 inches, very favourable for burning 7 cwt. of 48-per-cent. Spanish ore, charging once every 24 hours.

The just-mentioned rate of burning equals 30 lb. of 48-per-cent. pyrites per superficial foot of grate in 24 hours. With poorer ore

(40 to 42 per cent.) the author has certainly burnt in the same grate 8 cwt. (=35 lb. per square foot), and with 38- or 40-per-cent. ore even 9 cwt. (=nearly 40 lb. per square foot). In England the maximum quantity of pyrites burnt per square foot of grate will very rarely exceed 40 lb. of 48-per-cent. pyrites; reliable figures from one of the largest works are 35½ and 39 lb. But in German works, according to Hasenclever, using Westphalian pyrites, the proportions are 41·6, 44·5, 57·8, 60·3, and 65·0 lb. (Wagner's Jahresb. 1871, p. 212). Bode (*ib.* 1874, p. 245) quotes for Westphalian pyrites of 41 or 42 per cent. 50·7 to 64·0 lb.; for Norwegian ore of the same strength, 38·3 lb.; for Valais ore, with 35 per cent. sulphur, up to 92 lb. per square foot in 24 hours. Favre (Monit. Scient. 1876, p. 271) states as the most favourable ratio in his experience 55·3 lb. of 40-per-cent. pyrites per square foot in 24 hours.

At the Oker works, according to Bränning, the total grate-surface of eight burners belonging to a set of chambers of 65,500 cubic feet capacity amounted to 226 square feet—that is, 1 square foot to each 290 cubic feet of chamber-space, with a depth of 1 foot 6½ inches pyrites over the grates. There are daily 3½ tons of 40-per-cent. ores burnt, equal to 30·5 lb. per square foot of grate, which agrees much better with the author's results than with those of Hasenclever and Bode.

It is hardly necessary to say that the pyrites-burners are always built in sets. Usually 12 to 24 burners are served by the same set of men; and they must be worked so that every one gets its regular turn, as is evident from the necessity of a regular evolution of gas. Frequently the burners are built underneath the acid-chambers. Not only must they in any case be protected against rain (if not underneath the chambers), but they must not stand in a space open at the sides, since strong winds would put their draught wrong, and cause them either to go too fast or too blow out of the doors. It is best to protect them by light walls or by a brattice with shutters adjustable according to the direction of the wind.

As the drawings of the English burners will show, each burner is independent of the other, and they do not communicate with one another, but only with the common gas-flue. Each burner, then, ought to have its own damper, which is not always the case. On the Continent, frequently the single burners are only separated by low walls; the whole set is then like a large burner with a divided grate; but it is not possible, as on the English system, to treat each burner individually, and give it more or less draught, or isolate it for repairs. This system, therefore, cannot be recommended.

In continental works possessing no Glover tower it is very usual to concentrate the chamber-acid up to 144° Tw. in *lead pans*, which are mounted on the top of the burners, and are heated by their waste heat. Of all plans for concentrating vitriol this is, as we shall see later on, the cheapest, only excepting the Glover tower. There is no reason why such pans should not be placed on the English burners as well; but even before the Glover tower did away with all lead pans, the above arrangement does not seem to have been practised in England. In this country, however, the space on the furnace-arch is otherwise usefully employed for drying "balls" from pyrites dust, &c. There are also, as we shall see, some reasons against placing the pans on the top of the burners.

The *"potting" of the mixture of nitre and sulphuric acid* (liquid nitric acid is not used in England for this purpose) has latterly nearly always been done in such a way that the burners are not disturbed by it. Even ten or twelve years ago the pots were frequently put on pillars between two burners, with a common gas-space; to these belonged special potting-doors in the burner-front, and cast-iron dishes as saucers for receiving the stuff that boiled over; these saucers had some fall towards the doors, so that the nitre-cake could not so easily run into the burners; but it got out of the doors, which made them look very dirty; and ultimately it also got into the burners themselves. None of the better factories have this arrangement now, but all pots belonging to a set of burners are placed in a separate "nitre-oven," which is nothing but an enlargement of the gas-flue, and either situated over the burners or on pillars outside the same. The latter is preferable; for also here there is always a metal saucer provided for catching the boiling-over nitre-cake: this may be cracked before it is noticed, and much nitre-cake may get into the burners, doing great damage. If the arrangement is similar to fig. 53 (where, by the way, the nitre-pots are replaced by a better contrivance to be described hereafter), no risk of the above-mentioned kind is run.

Favre (*l. c.*) reports that the works in the south of France still use pots of 2 ft. 7½ in. × 1 ft. 6 in. × 12 in., standing on a bridge between two burners; and he also mentions the drawback of boiling over into the burners. This would show that those works, even in 1876, were in a backward state.

We shall now give diagrams of different kinds of *pyrites-burners* such as are usual now-a-days in England. Figs. 50 to 52 show a simpler construction, which can be made with open sand castings; figs. 53 and 54 a more expensive kind of front plates, requiring planing, turning, &c.: the latter are much neater and cleaner, because no putty is required for the doors. To be sure, sometimes these front plates become a little warped; and then the doors are not tight without putty.

Fig. 50.

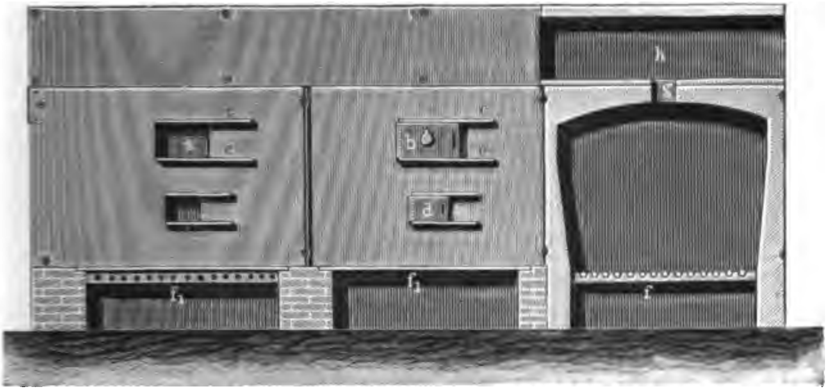


Fig. 51.

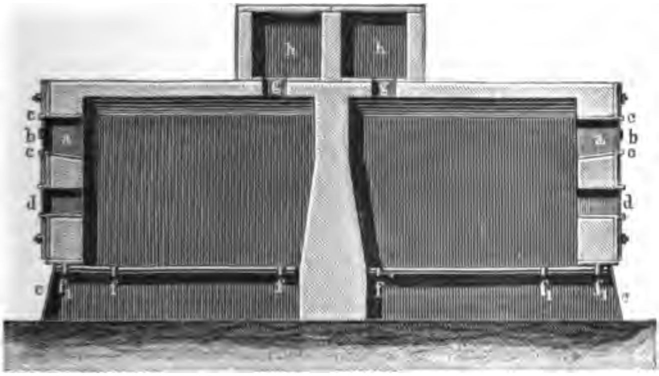
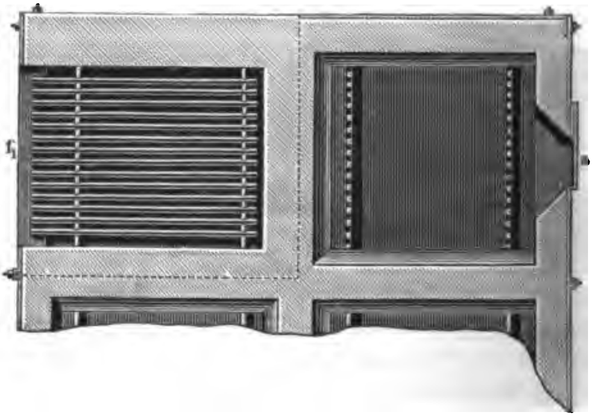


Fig. 50 shows two burners in front elevation, and one in section, the first burner without doors. Fig. 51 is a cross section, showing two rows back to back; fig. 52 a sectional plan, half taken just over the grate, half through the middle of a door. *a* is the working-opening, with the door *b*, which slides in the grooved ledges, *c c*, cast to the front plate. The small door *d*, only to be used exceptionally, is arranged in precisely the same way. The openings of the brickwork inside are protected by small metal plates; *e* is the movable cover of the ash-pit, provided with air-holes; *f f* are the grate-bearers; the front bearer *f* at the same time carries the bottom plate for the front wall, and is perforated by round holes; whilst *f f* are cut out in semicircles. The arches are sprung parallel with the working-doors, and, by the draught-holes *g g*, are in connexion with the gas-flues *h h*. The latter, like the burners altogether, are cased in metal plates; they are covered by fire-tiles.

Fig. 52.



A somewhat more costly but more perfect arrangement is shown in figs. 53 and 54, in front elevation and two sectional elevations. *a* is the working-door, with the small slide *b* for observing the interior of the burner; it turns on hinges, and, as shown in fig. 54, lies on a projection of the front plate, slanting forward towards the bottom; all the metal parts coming into contact are planed and faced, so as to close air-tight. Just in the same way the doors *c c* for the grate and *d* for the ash-pit are made, whilst the rarely used doors *e* and *f* (the latter for the gas-flue) are made in the same simple manner as in fig. 50. The burners are supposed to be the last of the row; so that the nitre-oven *g*, with the semi-cylindrical trough *h*, the saucer *i*, and the hopper *k* are immediately joined to them. The diagrams are all on a scale of 1 to 50.

Fig. 53.

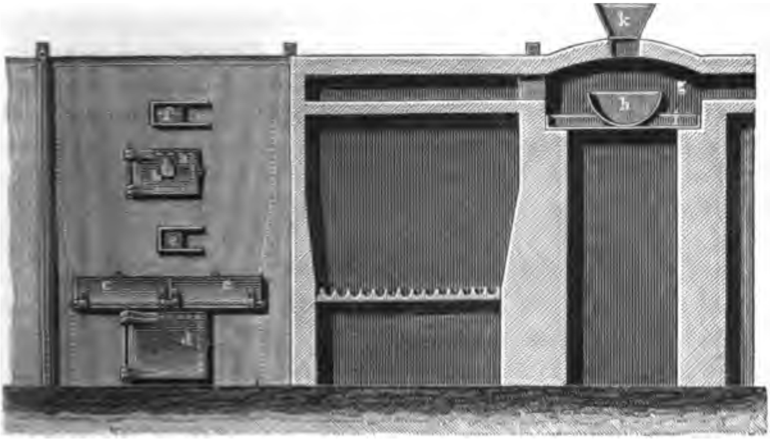
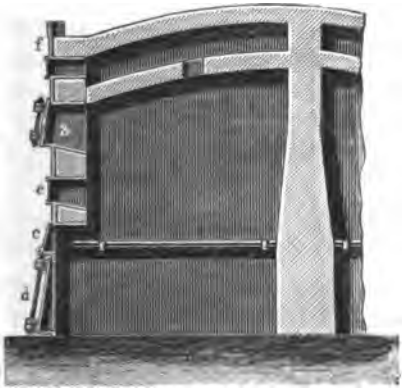


Fig. 54.



Working of the Pyrites-burners for Lumps.

In order to *start a burner* it is first, if newly built, dried by a slow fire in the usual way, and then filled with burnt ore to within 3 inches below the working-door. If no burnt ore can be procured, ordinary road-metal &c. can be taken, broken sufficiently to pass between the grate-bars when they are turned. The draught-hole of each burner is closed by a damper, and the working-door is left open. Then ordinary fuel, wood or rough coals are heaped on the ore and lighted. After twelve or twenty-four hours the burner and the uppermost layer of the ore will have reached a red heat; the rougher parts of the fuel still present are then drawn out and an ordinary charge of green pyrites is put on. By the heat of the burner-walls, that of the ore below, and the fuel still present, the fresh ore will soon be lighted; when it is fully burning, the working-door is closed, the damper closing the access to the gas-flue is opened, and the gas allowed to go to the acid-chambers.

Thus the process is started; and it is now continued regularly and uninterruptedly till it has to be stopped for external reasons. Repairs are very rarely necessary in pyrites-kilns; but those of other connected apparatus may compel their stoppage. Some few English works put in the dampers every Saturday at midnight, and only open them at Sunday midnight; in the mean time all other openings are well closed; and the burner thus keeps its heat so well that the new charges at once take fire when brought in. If any temporary interruption of work does not last beyond four or six days, usually the burners can be kept hot enough in this way to be started without any fresh lighting-up by means of fuel.

The regular burning-process has a double object, from which all the precautions to be observed follow. In the first place, the sulphur contained in the ore is to be burnt as far as possible; and, secondly, a just sufficient quantity of air is to be employed, no more and no less than is required for the chamber-process. This means, besides the air necessary for burning the sulphur to sulphurous acid, as much more air as is required for oxidizing the latter to sulphuric acid, and, moreover, a certain excess of air found necessary in practical work. Anyhow, therefore, the air will be more than just sufficient for burning *all* the sulphur contained in the pyrites;

and the second condition seems thus to imply the first. But this can only be said for brimstone and for pure pyrites not containing any zinc blende or galena &c.; for only the former can be desulphurized completely by their own heat of combustion. The sulphates of iron, which are always partly formed as intermediate products, are decomposed again at a comparatively low temperature into Fe_2O_3, O, and SO_2, or into Fe_2O_3 and SO_3, for which the heat of the burners is quite sufficient. This is a little more difficult with the sulphides of copper; but the temperature of decomposition of $CuSO_4$ is also within a red heat. Moreover the copper-extraction works do not want all the sulphur to be burnt, but allow a residue of from four to at most six per cent. sulphur in the cinders. If, however, the ores contain blende or galena, which on burning are transformed into zinc and lead sulphates, the burner cannot possibly effect a total desulphurization; for these sulphates are only decomposed at a strong white heat, which is not allowable in a pyrites-burner, and they must thus remain as such in the cinders. Furthermore, if the pyrites contains calcium sulphate or carbonate, a corresponding quantity of $CaSO_4$ will remain in the residue. Any barium sulphate present would not be taken notice of in the testing of the pyrites or the cinders, being classed among the "insoluble."

If we leave unnoticed the ores containing much zinc or lead, and only speak of the usual descriptions of pyrites, the burning of ore in lumps will reduce the sulphur in the cinders with good work to 3 or 4 per cent. Less than 3 per cent. of sulphur very rarely occurs on an average of the whole year; the contrary assertions of many managers, if questioned upon this point, are refuted by the analyses of the copper-extraction works, which, according to Wedding and Ulrich (Wagner's Jahresb. 1872, p. 156), in 1871, found 3·66 per cent. on the average. Most frequently the limit stated above for good works is exceeded; many works leave 6 or 8 per cent. of sulphur, and even more, in their cinders, whilst their neighbours only leave 4 or 5 per cent. in the same ore. The fault of this may be either with the description of burner employed or with the style of work. If, by the construction of the burner, the pyrites lies in too shallow a layer, and this is let down too soon on shaking the bars, it will easily come out badly burnt. But even if the burner is quite rightly built, much still depends upon the skill and care of the burner-men. If these do not work up the ore through the door-way with strong pokers, if they do not charge it equally all over, slanting about 2 inches towards the door from the back and the sides, if they shake the grates unequally, so that the ore comes down more quickly in one place than in another, if the ore is put in in too large pieces, and so forth, no proper burning can be expected. The latter is also intimately connected with an avoidance of "scarring," which depends upon a proper supply of air, to be spoken of directly.

Whether pyrites is properly burnt or not can be recognized to a great extent by the eye. By the burning-process the pieces swell out and burst in some place; they become light and porous, and assume the red colour of ferric oxide, in the case of cupreous pyrites a more blackish red colour. The burnt ore ought therefore to consist of light porous pieces of the proper colour, apart from the powder always present in large quantity, which is generally sufficiently burnt off. Already, on taking up the larger pieces, their weight will allow a rough judgment of the state of the burning; and this can be more distinctly recognized by breaking the pieces and observing whether they contain a raw core in the centre. Also the presence of many slags (scars) on the cinder-heap is a proof of bad burning.

Important as these empirical signs are, no well-managed factory will be satisfied with them, but will from time to time, daily or at least twice a week, have the cinders tested, after having drawn a large sample and reduced it properly. At all events the above-mentioned empirical signs have hardly any value for smalls.

The chemical testing of pyrites cinders (*burnt ore*) takes place by exactly the same methods as described in the fourth Chapter for the analysis of pyrites itself. Although in this case the utmost accuracy is not required, and short methods might be properly employed, there do not seem to exist any sufficiently reliable. Even for this purpose the method of Pelouze is useless, as has been proved by many tests of the author's and of his former colleagues. But when using a quick mode of filtration, such as the long funnel described on p. 104, a cinder-testing can be finished in little more than an hour, if the finely-powdered ore (2 or 3 grms.) be treated for five minutes with hot aqua regia, evaporated till just dry, diluted with a little HCl and much hot water, filtered, and the sulphuric acid in the solution estimated volumetrically or even gravimetrically.

The sulphur contained in the burnt ore is most probably not present as FeS_2, apart from any quite raw cores in large pieces. But even the fine or quite porous cinders, burnt as well as possible, also those from pure pyrites free from lead, zinc, and lime, always contain sulphur; and as this cannot well be in the shape of FeS_2, the question can only be whether they contain FeS or sulphates of iron (most probably basic ferric sulphates), or both. According to Scheurer-Kestner and Rosenstiehl (Bull. Soc. Chim. 1868, ix. p. 43), the cinders contain essentially FeS; they give two analyses—(i) of properly burnt ore, (ii) of on operation carried on too hot, so that the ore had fluxed. Both are from Sain-Bel pyrites, containing 46·1 per cent. sulphur in the pieces and 49·28 in the smalls.

		I.		II.
Moisture		1·0		
FeS		8·5		27·2
Fe	5·4		17·3	
S	3·1		9·9	
Oxide of iron		72·0		62·4 *
Fe	50·4		41·0	
O	21·6		21·4	
Quartz		18·5		10·4
		100·0		100·0

According to these analyses there would be no ferric sulphate whatever in the residues, which is very improbable, as such can be proved by washing with water (comp. Bode, Dingler's Journal, ccxviii. p. 327, and further analyses by Phillips, Gibb, Bräuning, Wedding, and Ulrich in the 16th Chapter).

Richters (Dingl. Journ. cxcix. p. 292) gives the following analysis of burnt ore from the Silesia works at Saarau:—

Water	4·35
Iron	43·36
Manganese	0·16
Silica	13·92
Alumina	4·84
Lime	0·02

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* The calculation does not agree here; 62·4 Fe_2O_3 would contain 43·68 Fe.

Zinc oxide	8·83
Sulphur trioxide	4·35
Sulphur	1·53
Oxygen and loss	18·64
Nickel and arsenic	traces
	100·00

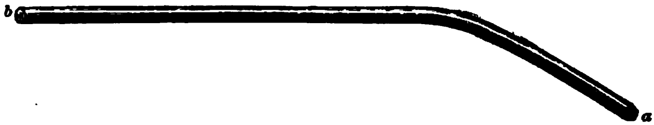
Phipson has published the following analysis of residue from Irish pyrites (Chemical News, vol. xviii. p. 29):—

Zinc oxide	5·50
Cupric oxide	2·86
Manganese oxide	1·60
Nickel and cobalt oxide	0·12
Cadmium oxide	0·01
Lead oxide	1·67
Antimony oxide	0·04
Ferrous oxide	1·17
Alumina	3·25
Sulphur	2·60
Thallium	traces
Indium	traces
Gangue	15·00
Ferric oxide	65·99
Lime	0·11
Magnesia	0·08
	100·00

Every thing that has been said on the maximum of sulphur in the cinders to be aimed at, only refers to the burning of pyrites proper—that is to say, of ores containing essentially FeS_2, and got exclusively as a raw material for vitriol-making, in which case the cinders are as good as worthless. Just in the same line are those cupreous pyrites (with up to 4 per cent. of copper) whose copper can only be extracted by the wet process; for these the above-mentioned rules for the sulphur in the cinders are equally valid. But the case is quite different with a number of ores where the residue from the burning is regarded as by far the most important product, and where the gas is only a by-product, often only converted into sulphuric acid in order to get rid of it. To this category belong blende, copper-pyrites, coarse metal, &c. Here the burning-down to the above-mentioned minimum of sulphur is partly not possible, partly not even desirable (as for copper-pyrites); and there exist for each case definite rules, which, however, do not belong to the domain of acid-making, but to that of metallurgy. For that matter, even where a larger percentage of sulphur is required for further metallurgical operations, it is more rational from the standpoint of the acid-maker, in order to save labour, burner-space, &c., to burn the material as well as possible, and to supply the necessary sulphur afterwards by adding a little green ore; thus, for instance, the copper-extraction works proceed when they receive the cinders too far desulphurized.

We now pass on to the second fundamental condition of proper work in the pyrites-burners, viz. *that neither too little nor too much air be employed.* At this stage we leave out of consideration the absolute quantity of air required, and only treat of the practical rules and of the appearances observed in the burners themselves. If too little air is admitted, whether from too few holes in the bottom door being opened, or from the damper in the draught-hole not being enough drawn, or because the pipes are stopped up with dust, or the draught in the whole chamber system is insufficient from one cause or another, the same thing will happen as with sulphur-burners when they get too hot: sulphur will sublime as such, and will be deposited in the flues, the dust-chambers, the Glover tower, or the chambers themselves. It is, however, a more frequent and serious consequence that, in the case of insufficient draught, the often-mentioned *slags* or *scars* are formed. These, as Scheurer-Kestner and Rosenstiehl have shown (*l. c.*), consist mostly of *iron monosulphide*, FeS, which is necessarily formed when FeS_2 is heated with exclusion or insufficient supply of air, along with free sulphur. It is easily fusible, and fluxes in the burners to more or less large cakes or scars, upon which the air has practically no action. The FeS fluxes all the more easily, as in the case of insufficient supply of air, where no cooling by the excess of air takes place, *locally* more heat is developed than when the supply of air is abundant. The scars mostly enclose some green pyrites, and in this way also cause a loss of sulphur. A much greater loss is occasioned by their stopping the passage of air, so that the ore above and below a scar is very incompletely burnt. The heat is locally increased and driven further down than it ought to be; the zone of combustion is removed further downwards; and on letting down the ore the pyrites partly comes out incompletely burnt. If scars have formed in the burner, they naturally descend as the cinders are let down, and they would ultimately lie immediately on the grates and entirely stop them up. This, however, must at any rate be prevented. A careful workman always breaks up the surface of the old ore before putting in a fresh charge; and thus he finds out whether any scars have formed, which mostly takes place near the surface: they can then be easily brought to the surface by means of hooks and pulled out at the door. But if they have been overlooked at first and have got lower down, in doing which they constantly increase in size, their removal is more difficult. Then a very large and heavy poker of the best tough iron (these are made up to 12 feet long and 2 inches thick), bent in the way shown in fig. 55, is introduced into the burner through the charging-hole, and the men work it till they have got the point *a* underneath the scar. Several men, working at the end *b*, then try to lift up the scar, in spite of the resistance of the superjacent mass of pyrites. This labour is very disagreeable, exhausting, and difficult. The middle doors, between the charging-door and the grate, found in all pyrites-burners, are only used in extrême cases.

Fig. 55.



Apart from other causes, the supply of air in a burner may be insufficient because the ore lies too deep. As the depth of the ore depends upon the vertical distance between the grate and the working-door, it follows that for ores behaving very differently in this respect differently built burners must be used. Thus the deep burners built for Irish pyrites had at once to be given up when Spanish pyrites began to be used. With the same height of pyrites which was just right for the poor ore, in order to keep the heat better together, the rich cupreous ore, in itself more fusible, became far too hot, and, moreover, the air could not pass through quickly enough to make a *complete* burning of the ore possible at every point; from both causes combined followed this effect (easily comprehensible after what has just been said), that the scarring became excessive. It is always much more feasible to burn poor ore in a shallow than rich ore in a deep burner. Insufficiency of draught, if very considerable, will be easily recognized by the gas blowing out of all the joints of the burners, and especially coming out in force whenever the working-doors or the bottom door are opened. On the other hand, the draught is not to be so strong that too much air will get into the chambers; the gas ought to be kept as rich as possible, as will be shown hereafter. It may be assumed that the draught is just right, if, on opening the small slide in the working-door, neither gas nor flame issues from it, nor, on the other hand, the flames inside the burner perceptibly tend towards the draught-hole. They ought to rise up perpendicularly and quite steadily; and on opening the door, they may even tend slightly towards it. As, however, the exact regulation of the draught can only be effected by regulating the holes in the bottom door, and as on each opening of the doors above or below the grate much more air must get in than is necessary, of course the times during which the doors are opened are restricted as much, and the charging, shaking of the grates, and discharging are managed as quickly, as possible. It is very advisable to close the holes in the bottom door completely while the top door is open. If the draught is not very abundant, whenever the door is opened, there will be no room for so much air rushing in, in consequence of which a portion of the gas will rush out and get into the burner-house; this is both a loss, and a nuisance to the workmen, and, in greater quantity, also to the neighbours.

For regulating the supply of air several plans are possible. The regulation takes place either *before* the grate, by the holes in the bottom door, or *behind* the grate, by means of the damper in the draught-hole or that in the large chimney behind the chambers. The latter is only available where all the burners have a common gas-space; otherwise the draught through the chimney must be equal to the maximum amount required for all the burners, and must be changed according to the atmospheric conditions, each burner being regulated separately. This could be done best and most safely by the dampers in the draught-holes connecting each burner with the gas-flue; but these are rarely used for this purpose; they would have to be made very tight-fitting, and then would easily be set fast by flue-dust. Therefore here also the draught is made sufficient for all eventualities. The real regulation of the air, at least generally in England, takes place by means of the holes in the ash-pit door, of which a sufficient number are closed by plugs or otherwise. Scheurer-Kestner went so far as to pass all the air through a Comte's anemometer; but this can only have been done for isolated experiments, since such a delicate instrument can hardly have been kept fit for use for any length of time in an atmosphere thus exposed to acid vapours and to dust. It is therefore left to the burner-men to open or close the holes in the door as required.

The supply of air is usually regulated by the following practical rules:—At the beginning (that is, immediately after making a fresh charge)the burner does not want very much air, till the ore has caught fire, which will take half an hour or an hour. Then more air must be admitted, always with the above-mentioned restriction—that the flames rise perpendicularly, and tend slightly towards the slide when this is opened. When, however, the principal portion of the sulphur is burnt and the flames become scarce, the air is altogether shut off, and further action is left to the heat of the burner. About two hours before it is time for recharging, the working-door is opened and the ore is well raked and turned over by means of a hook to a depth of 3 or 4 inches, and any small scars are removed. If herewith blue flames appear to any extent, this proves the burning not to have been sufficient, and a little air must be admitted. When the whole time is up, be it a twelve-hours' or a twenty-four hours' turn, the air is entirely shut off at the bottom, the small doors covering the grate-bars are opened, and these are turned two or three times, leaving each alternate one out. During this the workman must look through the working-door, to see whether the layer of ore is let down evenly all over; he can easily manage, by the judgment of the eye, not to let the ore down too much or too little. Then, as quickly as possible, the new charge of ore in pieces (usually with a little dust), which must have been lying ready in front of the burner, is put in, and the process begins again. It is evident that there must be a regular rotation, so that a fresh burner comes in turn every hour or so;

this is both indispensable for a regular evolution of gas and convenient for distributing the labour through the day.

The interior of a burner, after the throwing-in of a fresh charge, is, of course, at first quite black. Gradually small blue flames appear, which become larger and more lively and cover the whole mass. After a few hours they become scarcer again; but the mass in the mean time has become red-hot. Later on it cools again; and towards the end of the period there is no glowing visible at the surface; but as soon as the mass is stirred up, the glowing appears again.

The men like to employ a practical test, to convince themselves that the burner is not too hot for recharging, in the shape of strokes made with brimstone on the burner-door: so long as these take fire at once, the burner is still too hot; only when they remain is it cold enough for charging. Frequently it is necessary to wait a little, even for a few hours, after shaking the grate-bars and letting down the burnt ore, in order that the burner may cool a little before recharging it; this has the advantage that the top layer, by turning it over, is caused to burn its sulphur more thoroughly than it can be burnt after cold pyrites has been thrown in.

Generally it takes some time before the men get used to a new kind of burner or of pyrites. If even skilled men are taken from other places, they require special supervision, and still more if a new kind of pyrites has to be tried. If at all possible, different kinds ought not to be tried mixed up, but one kind adhered to for some time, because only in this way do the men get used to a thoroughly proper treatment of the burner. Each kind of pyrites requires a little different treatment as to supply of air, to breaking up, &c.

An extremely important assistance in regulating the burning-process is the analysis of the gas, which, however, is nearly always made for a whole set of burners together in their common flue. We shall enter into the details of this later on.

If a pyrites-burner is working properly, it will, if touched outside, be so hot in its upper part (say 6 inches below the working-door) that the hand cannot be borne upon it; further down it must be cooler; and immediately above the grates it ought to be cold, or at most hand-warm. *This is one of most important practical signs of the proper working of the burner.* If a burner is too hot below, this may be the consequence of insufficient draught, or (which in the end comes to the same thing) there has either been too much pyrites charged or there is too much dust in the burner, which has stopped up the interstices. Too much dust may come from bad riddling, from too much having been added on purpose, from the falling of the "balls" inside the burners, or from the decrepitation of "explosive" ores (comp. p. 100).

In any case, the first thing to be done, apart from doing away with the cause of the evil, is to *cool* again the excessively hot burner. Above all, *more air* must be admitted; and, in order to drive up the heat more certainly, the new charge must be kept back a little, and the fresh ore not put at all in the middle, but only along the sides and the back of the burner. It always takes one or two days, sometimes more, before a burner has recovered its normal temperature. In specially obstinate cases there is nothing for it but making very small charges for a day or two, till matters have come right again. Some manage by taking out the ignited top layer, allowing it to cool a little, and putting it back into the burner, which in the mean time has had more draught, owing to the lower depth of ore, and thus has cooled itself.

If a furnace is allowed to go too hot for any length of time, whatever may be the cause of it (want of air, too large charges, stopping up by dust, bad breaking up), the consequence will always be the same, viz. increased scarring with all its unpleasant accompaniments. The author has had to deal with cases where the scars became so copious that the burner had to be put out, the grates had to be drawn, the whole of the stone taken out, and the burner freshly filled up.

Of course it also happens sometimes that a burner goes *too cold* and the fresh charges take fire too slowly. This may be caused equally by a want of draught or by too small charges, and can be easily remedied in this case. If it has, however, got so far that the new pyrites will not take fire at all, nothing remains but putting in very hot ore from some of the other working burners; in this way the matter may always be put right with some patience, unless large scars are lying on the grates, or there are other serious faults, which must be done away with before proper working of the burner can be expected. A frequently used but objectionable remedy against cold burners is putting live coals on the pyrites.

Carbonic acid is a great enemy to the chamber process, probably not so much by diluting the gas (for its injurious action is far too great to be attributed to that alone), as by lying in the lower part of the chambers and preventing contact between the chamber-gas and the bottom acid, till it is removed by diffusion. This point, however, is not yet cleared up.

A pyrites-burner may also go too cold if there is *too much draught*, if, therefore, besides the air required for its intense working there is an excess, which only acts as inert cooling gas. This is a very great fault; for in this way the consumption of nitre is increased, and the yield of sulphuric acid very much diminished. Long before the burners cool from this cause, an excess of air may become injurious in this way; and by observing the flames in the burners (much better, however, by the analysis of the gas), it must be ascertained whether the proper proportion of air is present or not.

Balard reports ('Rapports du Jury International,' 1867, vol. vii. p. 29) that in the first trials of Perret and Olivier for employing pyrites in manufacturing sulphuric acid, they at last succeeded in properly conducting the combustion, but obtained a very small yield of acid. They ascribed this to an insufficient draught, and applied a fan-blast; but the yield instantly became minimal. Now the other extreme was tried; the air-channels were quickly stopped up with boards covered with sheepskins and fastened by stays. At once the chamber process became regular, and the key to employing pyrites in the manufacture of sulphuric acid was found. Probably the previous endeavours of Clément-Desormes in this respect were frustrated by his allowing too much air to enter.

Some have warned against the employment of *damp* pyrites (Kerl-Stohmann's 'Chemie,' 3rd ed. vi. p. 197), because in this case, on burning, more sulphates are formed, which give off sulphur trioxide; this takes up moisture, and condenses as sulphuric acid before getting into the chambers, destroying the flues and so forth. Even in damp weather similar phenomena are said to be observed, and a smaller yield is said to be the consequence of the moisture in the air. The author, on his part, has never noticed such an effect of damp weather, nor has he been able to learn any thing about it elsewhere, in spite of numerous inquiries. It would be desirable to examine this point specially. The formation of sulphur trioxide, as well as the occurrence of liquid sulphuric acid in the connecting tubes, certainly has been established; but that the moisture of the air acts in a way to increase that formation, has not yet been proved.

He who has no practical acquaintance with the matter, looking at these numerous sources of mishaps, may be inclined to think that the working of a set of pyrites-burners is a most difficult task. But it is far from that. If once the burners are in order, they remain very long so if the burner-men know and perform their duty to any considerable extent, and if proper supervision is exercised over them; the pyrites-burners then give even less trouble than sulphur-burners. To be sure, when they do get wrong, it takes energetic and experienced management to put them right again.

It will now hardly be necessary to explain in detail why there are only narrow limits for each given burner and style of charging, within which the *quantity* of pyrites charged may vary. If too much is charged, the burner scars; if too little is taken, it gets cold. When, therefore, for any reason the daily quantity of pyrites has to be cut down, it is necessary to put out a corresponding number of furnaces and to fully work the remainder. Only in the case of brief temporary interruptions is it possible to charge rather less than usual for a few days; but the author would recommend even in this case rather to allow the bulk of the burners to go on as usual, and to keep the necessary number hot without fresh charges by closing all openings. Then these furnaces will be much more easily put in order by the assistance of the other burners in full work than if they had *all* cooled down.

Thus far we have always spoken of the burning of pyrites *in pieces*. It is evident that the burning will be all the more regular the more uniform the size of the pieces is; but practically a rough approximation to this condition, difficult to fulfil strictly, is sufficient, such as has been stated above—viz., if no coarser pieces are amongst it than pass through a 3-inch sieve, and no smaller ones than are retained in a ½-inch riddle: where there are no special apparatus for dealing with dust, it is even possible to go down to a ¼-inch riddle; but, anyhow, the dust passing through this must be dealt with separately. This can be done in very different ways, according to circumstances. At works which do not buy smalls in that state, the question is only about the dust arriving along with the bulk of the ore and about that made in breaking. Much more dust is made when breaking by machine than by hand—in the former case up to 20 per cent. with middling hard ores, and even more with soft ores. Formerly, before rational and really satisfactory contrivances for the burning of smalls were known, some large works, which had already mounted Blake's stone-breaking machine, went back to the hand breaking, in spite of its costing three to six times as much, merely in order to avoid the excess of dust. This was especially the case with works using soft ores, such as the Tharsis ore; with Norwegian ores the advantage was always on the side of the mechanical breaking, because these are much harder and make less dust. If the quantity of dust going through the smaller riddle does not exceed 1½ cwt. to the ton, it can be got rid of, according to the author's experience, without any special contrivance, in the following way:—The dust is sifted off as usual, and a certain quantity of it is laid down for each burner alongside the pieces. If, for instance, the whole charge is 7 cwt., 6½ cwt. of pieces are used and ½ cwt. of dust; if more than this is used, the burner easily gets out of order. First the coarse ore is charged as usual; and then the man throws the dust with his spade along the *sides* and the *back* of the burner, leaving the whole central part free. Anyhow, the ore ought to be levelled with a hook, after throwing in the charge, in such a way as to make it higher along the sides and back than in the centre of the burner. The reason is this: the air entering from below meets with much less resistance at the comparatively smooth walls than in the centre of the layer of ore, and it will preferably rise along the former; the centre thus will get less air than the parts next to the walls. If, however, the latter lie at a higher level, and especially if the passage of air is obstructed by the dust lying at those places, the draught will be more nearly equalized, and the burning will take place evenly all over the area of the burner. Of course it is not well to proceed too far in this way.

The arrangement just described does not suffice if more than 1½ cwt. of smalls to the ton of pyrites has to be dealt with; and special arrangements must then be resorted to. Probably the oldest method, now almost obsolete in England, but not yet on the Continent, was the following:—The small ore is, without further grinding, mixed with sufficient clay to make it plastic, made into a puddle with water, formed into *balls*, and dried on a steam-boiler or pyrites-burner. Rarely less than 10 per cent. of clay will be required for this, often more, up to 25 per cent. The balls are then charged along with lumps into the ordinary burners, but never too many at a time (at most one sixth part of the whole charge), because they fall to powder in the burner after a time, and if used in a greater proportion would stop the draught. Only locally is such rich clay found that the balls stand pretty well in the burners and can be well burnt off. The workmen dislike them very much, because they disturb the working of the burners even when the above-mentioned restriction of their quantity is observed; if a burner is not quite warm, they must at once be left off. Some, in order to get rid of them without disturbing the burners, burn them by themselves, mixed with "coal brasses,"—that is, the pyrites picked out of coals, which always retains some of the latter, and therefore burns more vividly and gives out more heat than pure pure pyrites; but then it sends the injurious CO_2 to the chambers. Usually not much is gained by making the balls with clay, since they so quickly fall to pieces in the burner; and nearly as much can be done by throwing the dust at once into the burner and saving the cost of making the balls. Only by a very strong admixture of clay can the disintegration of the balls be prevented; but then the loss of sulphur and the contamination of the burnt ore is all the greater. In both cases the sulphur left in the burnt ore rises very much, from 6 to 8 per cent. and more. Where the cinders go to copper-extraction works, these usually prohibit the use of clay for balls.

These clay balls are connected with so many drawbacks, that something else was soon looked for. This was indispensable where nothing but smalls could be obtained, or where they could be procured so cheaply that acid-makers wished to dispense entirely or partially with using lump ore. At the pyrites-pits there are usually enormous heaps of smalls, which formerly were not saleable at all and would sometimes have been given away for nothing, just to make room. In other places pyrites only occurs in a loose, roughly crystalline shape; and, again, in others it is obtained by wet preparation altogether in the state of smalls. Thus there was great encouragement for constructing apparatus for burning small pyrites in large quantities.

The oldest contrivances for burning small pyrites by itself are *close furnaces* or *muffles*, the construction of which has several times been patented as a new invention. But, essentially, Spence's furnaces are identical with those of Imeary and Richardson; and long before both, Godin at Stolberg had used such; also the Belgian *fours à dalles*, mentioned in the Official Report of 1856, are nothing else. All such furnaces consist of a long muffle whose bottom, made of fire-tiles, is heated below by a coal fire, whilst on the top of it the pyrites dust is spread in a thin layer and is burnt by the air entering at several places, with the assistance of the heating from below; the sides and roof of the muffle are formed of brickwork; and the gas is conveyed into lead chambers as usual.

Concerning the shape of the furnaces, probably the worst was that of the Belgian *fours à dalles* (Belgian Official Report of 1856, p. 21). They had a surface of from 270 to 320 square feet, formed by flags resting on several longitudinal walls; below there were four or five fireplaces, divided over the length of the furnaces, and four or five working-doors in the muffle itself. The burnt ore was tipped into a cave by means of a hole in the bottom. The fresh ore was charged through a hopper or one of the doors. In twenty-four hours up to 5 tons of dust were burnt in six or eight portions; and it lay 4 or 5 inches deep. The operations of charging, burning, &c. took a great deal of time, during which the doors had always to stand open, and much false air got in. Every half-hour the whole layer, only burning at the surface, had to be turned over; and it is no wonder that the yield was here even worse than with the simultaneously employed *fours à grille*. The *fours à dalles* were justly prohibited by law, on account of the large escape of gas from them; and Chandelon in 1871 found none of them. The Report of 1856 recommends to the factories to use in their place balls made with clay; but this is not practicable for large quantities.

The furnace of Spence consists of a large muffle (figs. 56 & 57), similar to the Belgian furnaces, but, more rationally, only provided with *one* fireplace, *a*, at one end, whose flame travels along the whole length of the furnace in the flues *b*, *b*, and thus gives up its heat much better than could be the case in the Belgian furnaces. Spence's furnaces were from 40 feet long and 6 to 9 feet wide inside; but when heated, as in Swansea, by the waste heat of copper-smelting furnaces, their length was restricted to 30 feet. On the other hand, on the Tyne, even in 1873, furnaces of 100 feet length were in existence; but soon after they went out of use there. The great length of the furnaces was intended to save fuel. The crown of the arch is 15 inches above the furnace-bottom. Spence's furnace for 50 feet length has twelve working-doors, 12 inches long and 4 inches high (more, if longer), e, e', e''; the pyrites dust is put in through the door, e, furthest from the fire, only so much at a time that it can lie in layers of 2 or 3 inches in the space between two doors without getting mixed with the previous charge. When the whole furnace is full, the ore at e'' (nearest the fire-bridge), which has been the longest time in the furnace, is taken out by the opening f, the following charge is moved towards e'', and so forth, so that at e room is made for a fresh charge. The air is principally supplied by the discharging-channel f, where its volume can be easily regulated, as well as through the working-doors, which are only too often open. The gas goes through g to the acid-chambers. The ore thus first gets to the coldest part of the furnace, is gradually moved forwards towards its hotter part as it becomes poorer in sulphur, and at the same time meets air richer in oxygen—no doubt a very rational process, which, connected with good turning over, ought to permit a very good burning. If the

Fig. 56.

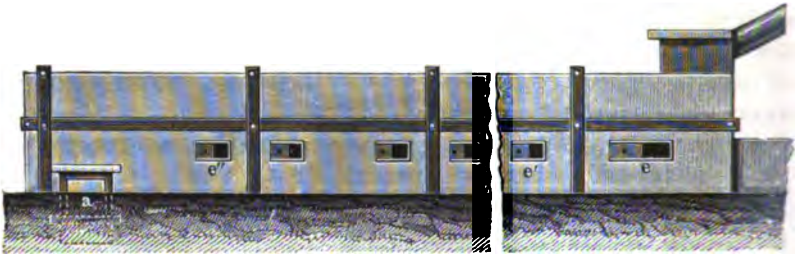
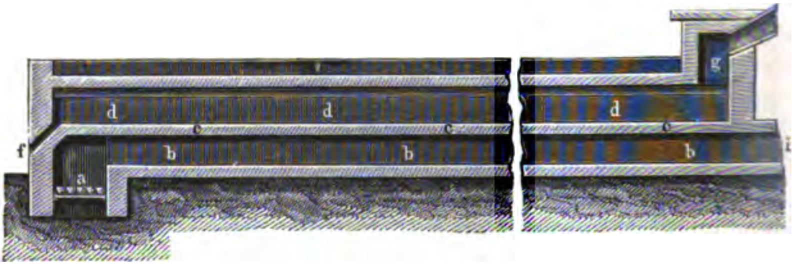


Fig. 57.



coarse parts are first sifted off, the inventor and the treatises state that only 2 per cent. of sulphur are left in the cinders; but the author knows that even with furnaces 100 feet long 7 per cent. of sulphur was the usual limit. If a fresh charge is put in every two hours, each of them will remain twenty-four hours in the furnace; each charge is 10 cwt.; that is, daily, 6 tons per furnace. Within the furnace an ample evolution of white vapours, consisting of SO_3, is noticed; this is either formed by the contact of the SO_2 and the oxygen of the air with red-hot ferric oxide, or more simply, and in this case more likely, by the decomposition of the ferric sulphate found in the cooler parts as it gets to the hotter ones. Spence points this out as a special advantage of his furnace, and even asserts that nitre is saved in this way; but he forgets that the only difference is this, that the vapours of anhydride can be more easily seen in the comparatively dark muffle than in a red-hot burner.

The drawbacks of Spence's and all similar furnaces, which have led to their being abandoned again, probably everywhere, are especially the following. As in the Belgian furnace, the turning over of the ore and its removal from one stage to another takes much time, which means much wages and much getting-in of false air; the latter must cause a large consumption of nitre (according to Richardson and Watts, vol. i. pt. v. p. 201, thirteen or fourteen parts to 100 of sulphur) and bad yield in the chambers. To this the consumption of fuel for firing must be added, which is stated differently, but amounts to at least half the weight of ore. If the flags of the furnace-bottom do not keep quite close, there is, according to the draught, either a suction of fire-gas into the chambers, or, more probably, of sulphur-acid into the fire-gas and thus into the chimney—one about as bad as the other. It is still worse if it is attempted (almost in vain) to lessen the consumption of fuel by making a double arch (which has been done at some works), and allowing the flame to circulate not merely underneath the bottom, but also over the roof of the muffle; in this case the likelihood of losing a great deal of gas by cracks in the furnace-roof is still greater. Lastly, also the quantity of residual sulphur is very considerable, unless the ore is finely ground before using.

Only for metallurgical purposes are such furnaces still in use, although even here (for instance for blende), latterly, better apparatus have supplanted them. But in these cases the residue is the main thing, the sulphurous acid only a secondary matter, and the convenience of keeping the former clean &c. is the paramount consideration.

A modification of the long muffle of Spence is that patented by Imeary and Richardson, in which the furnace-bottom is divided into a number of single hearths, each of them 4 to 6 inches higher than the preceding one nearer the fireplace (Hofmann, Report by the Juries, p. 14; Richardson and Watts, *l. c.*; Wagner's Jahresb. 1859, p. 137). The advantage of better keeping apart the individual charges will hardly make up for the greater complication in the construction; however, the furnace has been several times erected in this shape. A new modification of Spence's furnace (also employed a long time before him by Godin at Stolberg and at several other German works) consists in arranging several hearths one on the top of another. The work of moving the single charges forward certainly proceeds here better and more quickly. The access of air was to be diminished by rakes sliding in stuffing-boxes; but having got so far, the fireplace ought to be left out altogether, as Malétra's burner has shown (see below). The older German furnaces with several shelves did not work well at all.

After the drawbacks and the costliness of the muffle-furnaces worked by a coal fire had been clearly proved by prolonged use, the problem of utilizing the heat generated in the combustion of the pyrites itself for carrying out the process was taken in hand in several quarters. One class of apparatus for this purpose consists in a combination of burners for pieces and for dust in such a way that the heat generated in burning the pieces is used for burning the dust. To this class belong the simple plates over the ordinary burners, the burners of Perret and Olivier, and those of Hasenclever and Helbig.

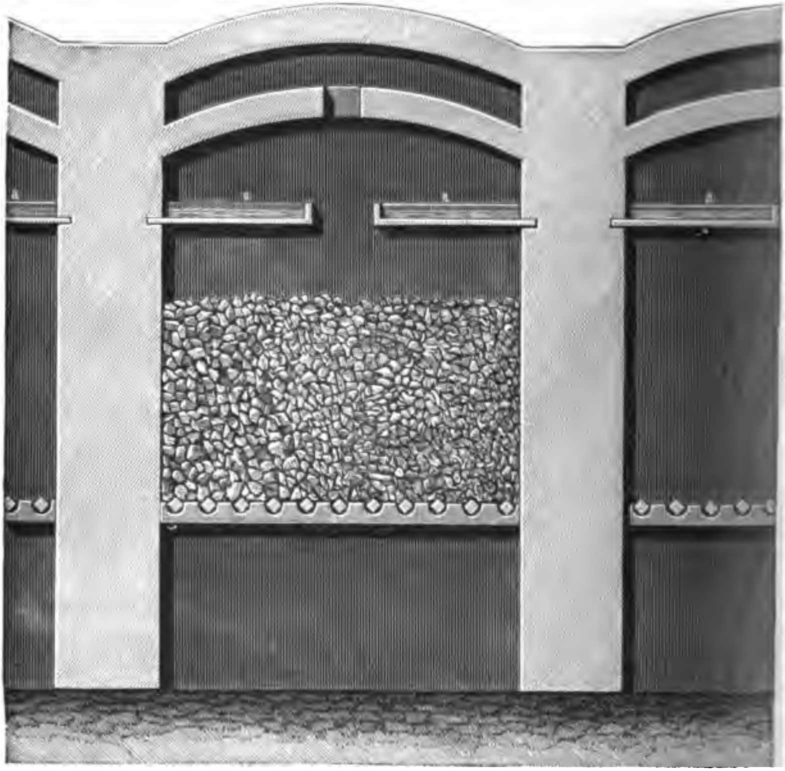
Another class of apparatus goes beyond this, and emancipates itself entirely from the use of pyrites in pieces, so that it is capable of more general use. To this class belong the burners of Gerstenhöfer, the new one of Hasenclever and Helbig, that of Malétra, and that of Macdougall—also that of Walter, which has a special application.

We must here mention a plan which does without any special dust-burners, and only represents an improvement (certainly of great importance) in making the balls: this we shall describe first. It is based upon the fact that pyrites, if in the shape of *very fine powder,* mixed with water *cakes together to a solid mass without* *the aid of any plastic substance.* This is caused by the fine pyrites dust, in the presence of water and air, beginning to oxidize very soon, even at the ordinary temperature; thus basic ferric sulphate is formed, which firmly cements together the separate grains of dust. This result only takes place to a sufficient extent if the grains of dust are very fine and the mixture with water very perfect; and this can never be attained by merely sifting and moistening the fine ore. The ore must therefore be ground finely with water in a mill, for which purpose usually the so-called *pug-mills* are used, a kind of vertical mortar-mill, sometimes with revolving bottom dish, or, if the dish is stationary, with a mechanical arrangement for throwing out the mixture as soon as it has reached the proper consistency. The pyrites smalls are thrown into the mill, water is run on, and the mill is run till a homogeneous mixture similar to fine mortar has been formed, which by itself has somewhat plastic properties. This mass is dried in layers of ½ inch thickness on the top of the pyrites-burners, often in cakes about 18 inches square; and after twenty-four or thirty-six hours it has hardened sufficiently for use. It is then broken up into pieces of the same size as the lump ore, and charged along with this into ordinary pyrites-burners. In this it is not necessary to observe a certain proportion; for the balls made in this way are so hard that they can be thrown to the ground without being broken, they do not fall to powder in the burners, and burn out as well as lumps; their cinders are, of course, of the same value as those from lump ore, whilst those mixed with clay make the utilization of the ferric oxide, at last obtained at the copper-extraction works, very difficult.

The only drawback of this process is this, that the mills suffer very much wear and tear from the hard pyrites. In spite of this it is general in the large English works, and has been reintroduced by those who had adopted Gerstenhöfer's or Macdougall's burners. The labour of grinding, carrying to the top of the burners for drying, taking down, breaking up, and laying down in front of the burners, amounts to 1*s.* 4*d.* per ton. To this must be added 6*d.* for coals for working the mill, and wear and tear of the same, altogether about 2*s.*, apart from the wages for the burning itself (another 2*s.* per ton).

The simplest plan for utilizing the heat of an ordinary pyrites-burner for burning dust is the placing of metal or fire-clay *plates* *above the burning lump ore,* and that only *in one tier.* In this case the burner is not changed in any material respect, but is only made somewhat higher, and its front plate is provided with doors for the dust-plates. Such contrivances, in one shape or another, have been used long ago; that which, for a few years, was much in use on the Tyne is stated by MacCulloch (Chem. News, xxvii. p. 125) to have been introduced by himself into Allhusen's works. The plates (which are visible in fig. 58 at *a a*) are divided into two halves for each burner, each of the halves having a surface of 1 ft. 6 in. × 5 ft., and 1 inch thick, resting in front, at the back, and at one side in the brickwork, and provided on the free side with a 3-inch flange for preventing the dust from falling off. A

Fig. 58.

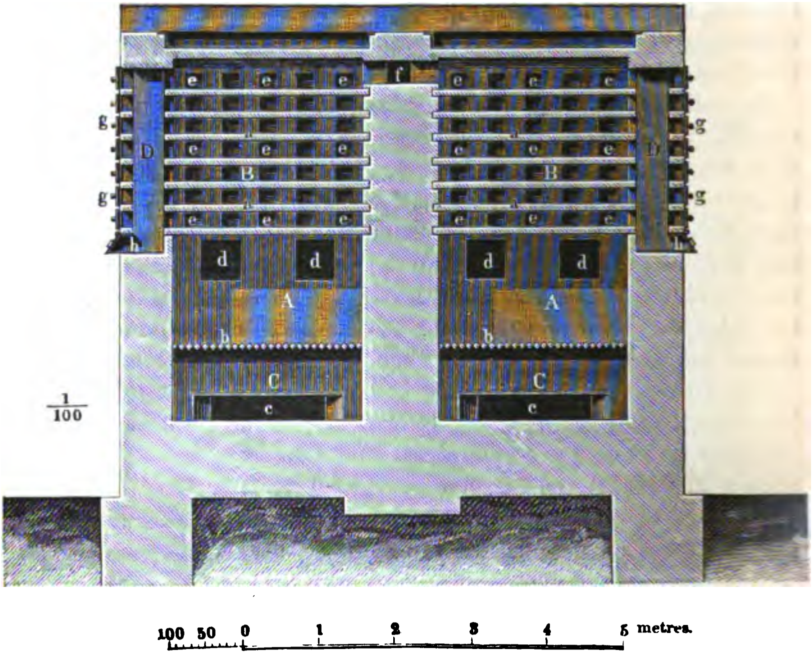


further support is given to the plates by a wrought-iron bar passing through the burner-roof; without this they would easily sag in the middle when red hot. Each half is served by a separate door in the front plate, which turns on hinges; and if one of the two plates is worn out, it can be replaced by another one in a few minutes after lifting out the door. This, according to MacCulloch, is only necessary once every six months; in reality it happens much more frequently. The doors principally serve for charging the dust by means of an appropriately-shaped spade, and for turning it once every three hours. Each plate receives 1 cwt. of dust, which is left on twenty-four hours; thus every burner can manage daily 2 cwt., with a charge of 6½ to 7 cwt. in the burner itself, of which up to 2 cwt. [?] may be dust also.

In spite of MacCulloch's assertions to the contrary, it must be stated, from the practical observations of those who have worked with such plates, that they have not been a success. The ore-dust is generally not sufficiently burnt in the 24 hours; on stirring it up much false air gets into the chambers; and the plates soon warp and become unserviceable. Plates of fire-clay are preferable, if they can be obtained to stand from the first. The plates sometimes, if too near the layer of ore in the burners, cool it too much. The wages for burning the dust on them amount to 4*s.* per ton.

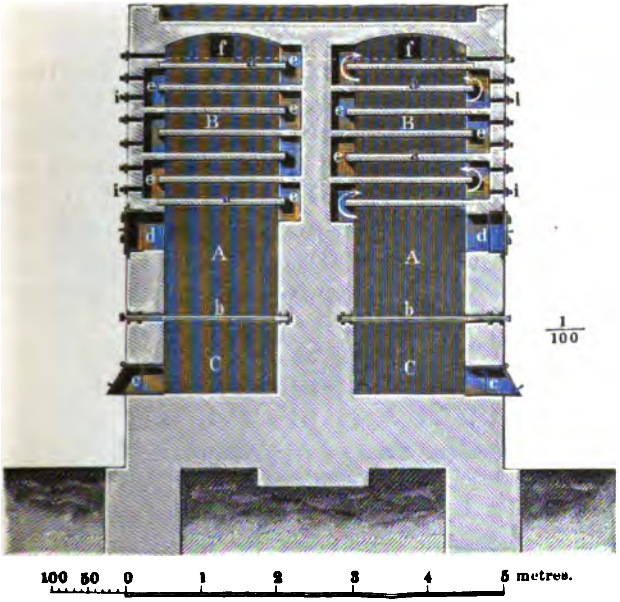
The principle of those plates had long before been carried out in a much more perfect way by Perret (the inventor of the first properly working pyrites-burners) and Olivier. Their burner is shown in figs. 59 and 60 on a scale of 1 to 100. Fig. 59 shows a sectional elevation in one direction, fig. 60 in another direction. Four of these burners are always built together so as to form an oblong mass; they work well only in this way, because otherwise too much heat is lost by radiation. In the lower space A the lump ore is burnt on a grate *b*, which in the diagram is represented as consisting of movable bars passing by means of stuffing-boxes through the front wall; it may, however, be in any other convenient form. C is the ash-pit, with the door *c*, through the holes in which the necessary air is admitted. The doors *d* serve for charging the ore in pieces. Up to this point we have got an ordinary burner before us; but above this there is an erection B for burning the dust. A number of fireclay slabs, *a*, 3 inches thick, are placed one above the other; the fine ore is put upon them in a layer of 2 inches thickness, and it is ignited and burnt off by the hot gas given off in the burner below. The latter travels by channels, *e*, left in the burner-wall, and visible in fig. 59 on the long wall, in fig. 60 at each side over each of the plates, as shown by the arrows in fig. 60; the newly formed sulphurous acid is carried along by the flues *f* to the acid-chambers. The small holes *i*, closed by clay stoppers, allow the burning to be observed. The openings *g*, closed by metal doors, serve for putting in the fine ore and also for drawing the same, after burning, into the channel D, formed between the doors and the plates along the whole width of the burner. During the working itself the channel D remains filled with burnt ore, and thus compels the gas to travel over all the plates. When these have to be newly charged, first the channel D is emptied through the door *h*; the latter is closed again, and the burnt ore from the lowest shelf drawn into the channel D, whose size is so arranged that it is just filled by the burnt dust up to the level of the fireclay plate. Now the lowest shelf receives

Fig. 59.



fresh dust, its door *g* is closed, and the burnt ore is drawn from the second shelf into the channel D, which thereby is just filled up to the level of this shelf itself. Thus the operation is continued till all the plates have been covered with fresh dust. According to Schwarzenberg such a burner allows of burning 65 parts of dust to 35 of pieces; but according to statements of actual work, only equal parts can be burnt. Usually lead pans are mounted on the top of the burners, in which, without any fuel, all the chamber-acid is brought from 112° Tw. up to 144°; but in several works, since the pans are easily melted by carelessness of the attendants, they are placed beside the burners and heated by the passing gas. The heat of the gas has also been employed for firing steam-boilers.

Fig. 60.



According to Michel Perret (Wurtz, Diction. de Chimie, iii. p. 141), if the layer of ore-dust is not deeper that 20 millims. (say ¾ inch), its oxidation is perfect down to the bottom without any stirring; the residual sulphur amounts to 4 or 5 per cent. both in the dust and the lumps (Balard, 'Rapport du Jury International,' 1867, p. 21; Scheurer-Kestner, in Wurtz, *l. c.* p. 142).

The burner shown in the diagrams has seven shelves and a height of about 20 feet above the ground-level; so that, in order to serve the plates, it must be half sunk in the ground and a pit made for it, which is very troublesome and causes much labour. This drawback has been avoided latterly by reducing the distance of the plates from 8 inches (as shown in the diagram) to 4 inches, and by employing only four shelves instead of seven (Perret had originally employed eight plates, and had then gone up to sixteen, arranged in two sets alongside one another; the gas was obliged to descend from the top shelf of one set to the bottom shelf of the other—a very objectionable arrangement). By this the burners have become much handier, viz. only 6 ft. 6 in. high, and they can now be entirely served from the ordinary ground-level; but, of course, less dust can be burnt in them. To be sure, in spite of the ingenious arrangement of the vertical channel D, filled with burnt ore and thus shutting off the gas, so much air is said to get into the burner in charging that, according to Balard (*l. c.* p. 22), 1 per cent. nitre to 100 sulphur is consumed in addition to that used with ordinary burners for lumps (?).

Olivier-Perret's burner, as we have seen, is not free from faults, and, moreover, has the drawback that it is tied to a certain proportion of dust to the lumps; but in spite of this it has been extensively employed in France, and not merely by the Société de St. Gobain, which had associated itself with Perret and Co. Outside of France it has been very little introduced; in England first the muffles, then the pugging of the dust, in Germany formerly Gerstenhöfer's and Hasenclever's burners have been preferred; and latterly Olivier-Perret's burner has been supplanted to a great extent in its own country by the so-called Malétra's burner. Where pieces have to be burnt along with a moderate quantity of dust, at most their own weight, the modified low Perret's burner can be recommended even now-a-days, especially as it makes less flue-dust than Malétra's.

The same principle which underlies the just-described burner is carried out in a quite different way in the burner of Hasenclever and Helbig, which is shown in figs. 61–63. It is a combination of a burner for lumps and another for smalls. The burners for lumps, *a a*, resemble very much the Belgian ones, and

Fig. 61.

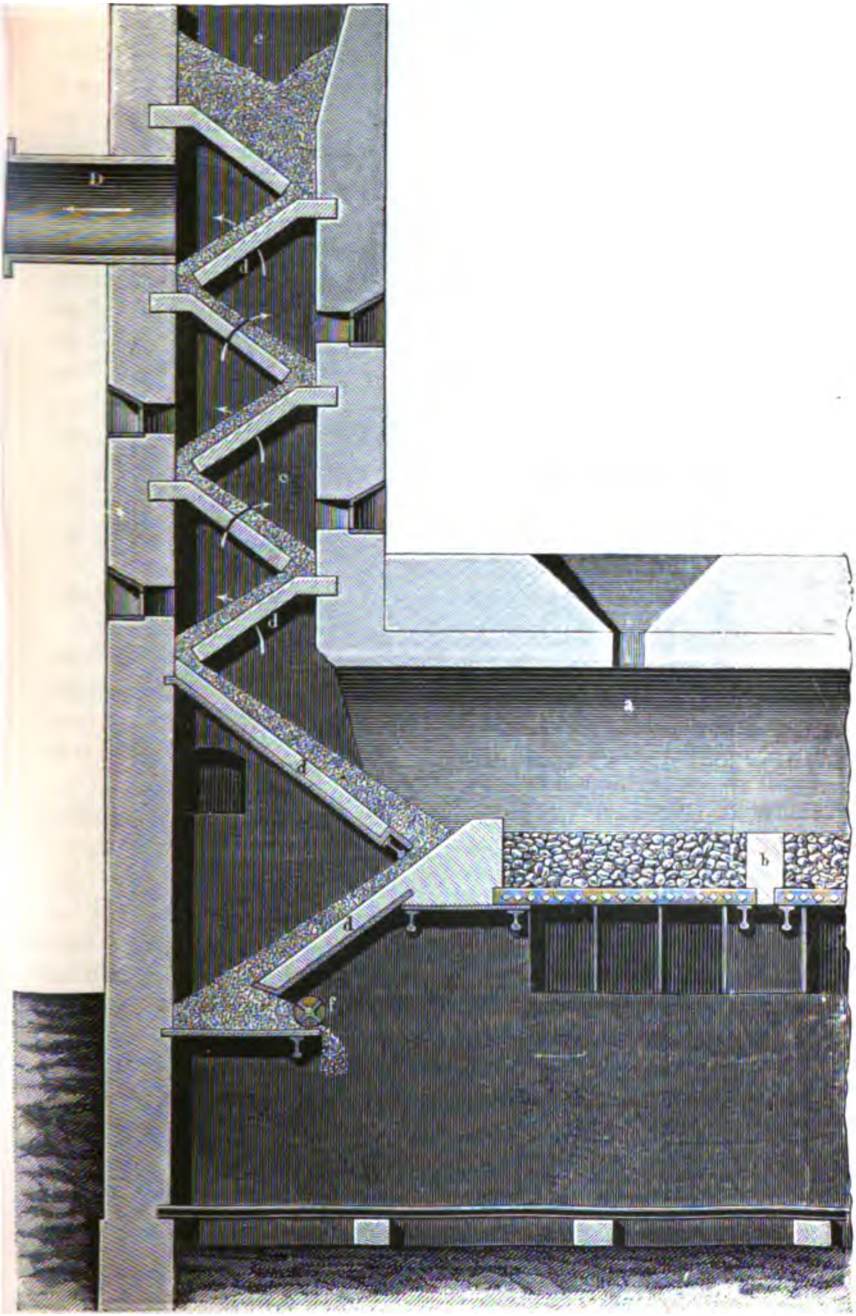
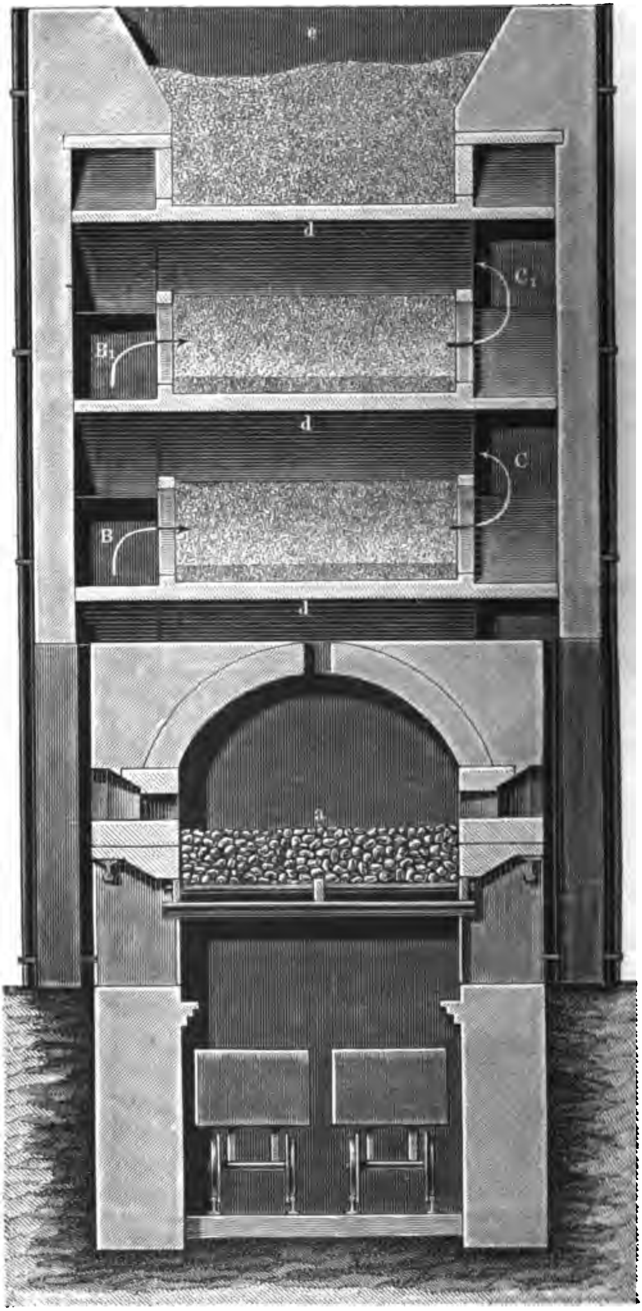
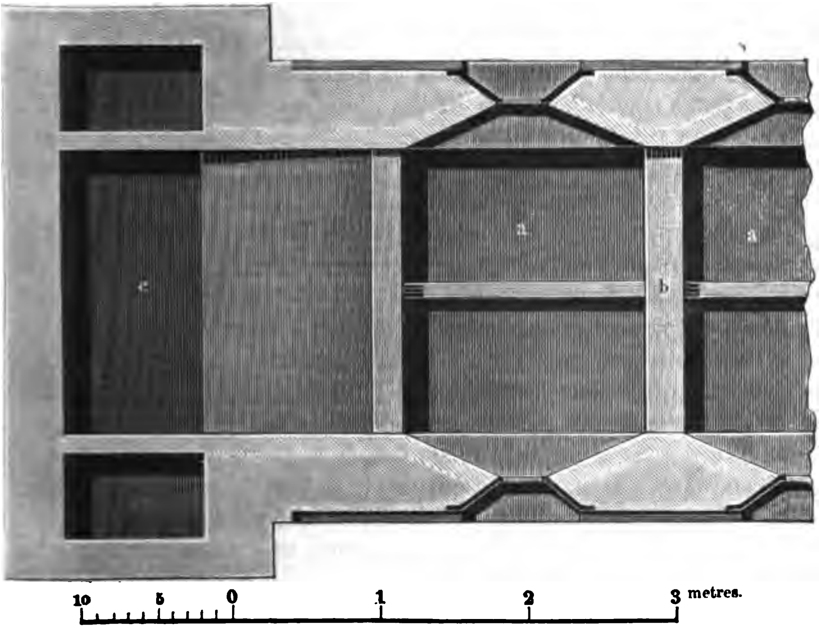


Fig. 62.



are properly one single burner whose grate, consisting of movable bars, is divided into four compartments by dwarf walls, *b b*. The

Fig. 63.



height of these, and accordingly that of the layer of ore, is only 1 ft. 4 in., which, for most descriptions of pyrites, is decidedly too little, but which could be increased without altering the principle of the apparatus. The gas-space is very high, and common to all the burners; the drawbacks of this arrangement have been already mentioned on p. 167. This, however, has nothing to do with the principle of dust-burning, as for this the construction of the burner for pieces is less material. The gas of the latter rises in a tower-like apparatus, in which eight shelves of fire-clay, *d d*, of a shape shown in the diagram, are placed. The free parts of the plates have an inclination of 38° to the horizontal, and cause the small ore (which may be a mixture of dust and "peas") to be burnt at the surface of its natural slope of 33°; the renewal of the surfaces of the ore and its passage through the apparatus are managed by taking away some burnt ore at the bottom by the roller *f*, either continuously or periodically, so that from above the ore must slide downwards after it from plate to plate. The fresh ore is first put into the hopper *e*, where it at the same time serves as a gas-lute for the burner-gas, and from this gets onto the first shelf, and, as more ore is taken away at the bottom, gradually onto the other plates, whereby its surface is continually renewed. The space below the shelves and above the ore serves as a channel for the burner-gas. The latter travels upwards in the direction shown by the arrows, first from B to C and on the next shelf from C to B, and thus in a zigzag motion at last arrives in the cylinder D, through which it is carried away to the acid-chambers.

This apparatus, in twenty-four hours, burns on the plates 15 to 20 cwt. of small ore of a size up to one third of an inch; on the grates in the four compartments 48 cwt. According to a later communication by Hasenclever (Wagner's Jahresb. 1874, p. 233), 10 to 16 cwt. of smalls can be burnt, generally down to 3·7 to 6·5 per cent. of sulphur in the cinders; the higher figures are reached in the cases of ore mixed with copper pyrites, galena, blende, &c. The size of the grain may reach ⅜ inch.

The Hasenclever-Helbig burners have been introduced in a large number of German and Austrian works, and were generally recommended. The greatest advantage which they seem to possess as against Olivier-Perret's burner, viz. the automatic movement of the ore, with continuous renewal of the surfaces, was not quite so great as it had been imagined, because the tower had to be looked after several times a day, and the sliding down of the ore had to be assisted by a thick iron wire. Sandy ores and "peas" slide well down; but floury ores are not well adapted for this apparatus, except when mixed with coarser grain. By separating the finer from the coarser pieces of ore, the burning of the latter is so much improved that it is possible to come down to 2 per cent. of sulphur against 5 per cent. when mixed with the peas and a little dust.

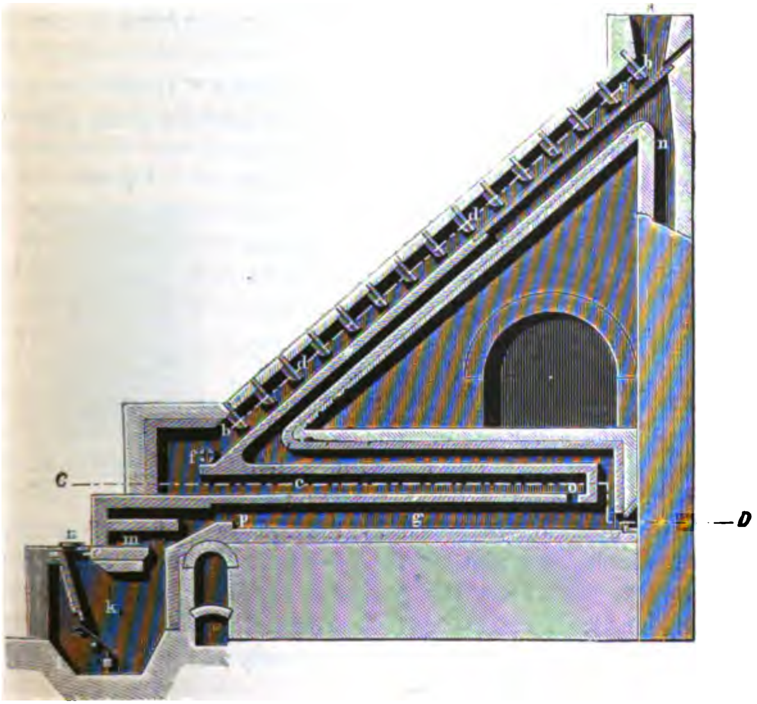
Usually the burnt ore in the Hasenclever tower is continuously removed by the roller *f*, which is automatically turned once every five minutes by a miniature water-wheel. At Liesing, near Vienna, every six hours intermittently the cinders of about 4 cwt. of ore are removed, which suits better for fine dust (Hasenclever, in Hofmann's 'Bericht,' 1875, i. p. 162).

This apparatus, as seen from the description, gets through much less smalls in proportion to the pieces than Olivier-Perret's; and it is accordingly only adapted for burning the smalls made in breaking, but not for working up smalls supplied alone. It is a great advantage of this tower that all smalls up to $\frac{3}{8}$ inch can be burnt directly without grinding.

In 1873, according to the French official Report on the Vienna Exhibition (ii. p. 5), already forty-six Hasenclever-Helbig burners had been built; but it does not appear how many were specially intended for sulphuric-acid making and how many were still at work. So much is certain, that the majority have been done away with again, to make room for the shelf burners on Malétra's system.

Several other constructions for burning small ore have been

Fig. 64.



indicated by Hasenclever, especially those adapted for blende—for instance, combinations of a muffle with an open roaster (Dingler's Journal, ccvi. p. 274; also in Hofmann's 'Bericht,' 1875, i. p. 168); we shall, however, only give that which is preferred by Hasenclever himself, in the diagrams figs. 64–67.

The ore is filled into a funnel at the top; and before getting into the muffle it must pass over a large inclined plane, heated from below by the waste fire of the blind roaster. If the ore were allowed to slide down freely on this plane, inclined at an angle of 43°, there would be formed at the end of this a heap more than 5 feet high, since finely powdered bodies, on being tipped down, form a nearly constant slope of 33°; thus a burning in the interior of the mass would be impossible. Therefore there are, at distances of 18 inches, partitions, *d d*, removed an inch or so from the inclined plane, and causing the formation of thin layers of ore along the whole slope. The partitions have a lateral opening, and are so mounted that the SO_2 from the blind roaster travels in the direction indicated by the arrows in fig. 67 a long way over the fine ore, and ultimately gets at *g* through a flue into a brick chamber. Thus the gas is made richer, and the ore is gradually burnt. The fire-flues below the inclined plane are readily accessible from the side, and can be easily cleaned during the working.

Fig. 65.

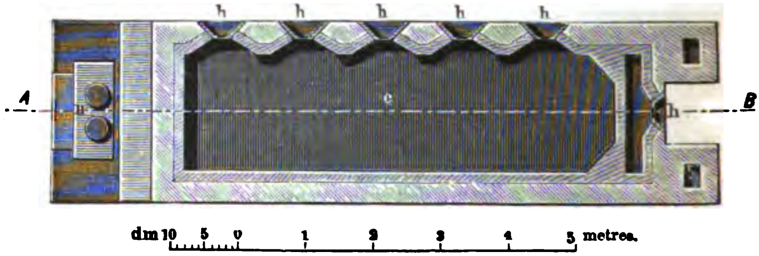
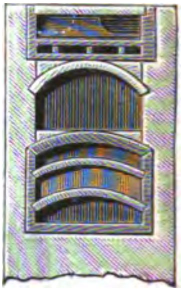
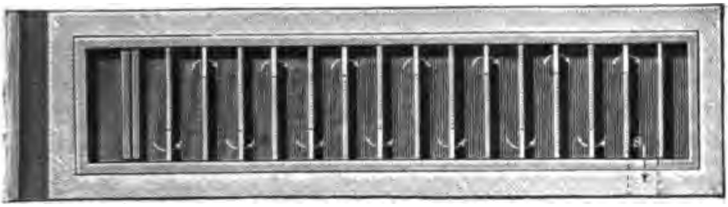


Fig. 66.



From the sloping plane the ore gets into the blind roaster by means of a roller at *f*, which is hollow, so that air can circulate inside and cool it. It is moved by a small water-wheel, and, according to the quantity of water, which is regulated by a tap, every two or 5 minutes throws a small quantity of dust onto the bottom of the muffle. By the movement of the roller the ore on the inclined plane is obliged to slide backwards. Every two hours the ore collected at the bottom is spread over the bottom of the blind roaster, and gradually moved forward till it gets to the opening *o*, and falls down to the hearth for burning it off by direct fire, The SO_2 given off on the bottom hearth is lost along with the fire-gas, whilst the gas from the blind roaster and from the inclined plane is used for the manufacture of sulphuric acid. The temperature of the furnace is so high that antimony melts in all parts of it. It utilizes even poor blendes with advantage; for an ore with only 20 per cent. sulphur still yielded gas with 6 per cent. of SO_2 by volume. There were in the ore:—

Fig. 67.



At the end of the inclined plane *b b* still . . .	10	p. c. S.
„ „ muffle at *o*	6·4	„
Burnt off at *p*	1·2	„

The reverberatory furnace is heated by a gas-generator *k*, in order to obtain a regular heat and save fuel.

These furnaces have been proved to be very well adapted for blende (Zeitsch. f. d. chem. Grossgew. i. p. 76). They are not only found at the Rhenania works at Stolberg, but also at Lethmate near Iserlohn, at Oberhausen, and at Schoppinitz in Silesia. They are said not to require more coals than ordinary open roasters (28 per cent. of the green blende), but 1*s*. 7*d*. more wages per ton, which is more than made up by the sulphuric acid. At Reckehütte, at

Schoppinitz in Silesia, there are eight such furnaces at work, each of which in twenty-four hours makes from 3½ tons of green blende and 2 tons of coal (this is about 60 per cent., not 28 per cent. !), 2 tons 15 cwt. of calcined blende with at most 1 per cent. of sulphur: three men per shift do the work. The most suitable grain of ore is ⅛ inch; coarser ore is calcined incompletely, finer ore does not slide down continuously, unless mixed with coarser grain. It gets from the blind roaster into the open one with 10 or 12 per cent. of sulphur. Each four furnaces are connected with a set of chambers of a capacity of 135,000 cubic feet, with Glover and Gay-Lussac towers, and in twenty-four hours supply 6 tons of vitriol of 50 per cent. = 4 tons of 66° Baumé.

At Lethmate, of the 32 per cent. sulphur contained in the blende, 20 per cent. are conveyed into the chambers as SO_2, 7 per cent. escape (likewise as SO_2) with the fire-gas, and 5 per cent. remain in the burnt ore, which is once more crushed between rolls and put back into the furnace (comp. also p. 113).

From a further communication of Hasenclever's (Dingl. Journ. ccxxvii. p. 71) it appears that now the average percentage of sulphur in the ore at the end of the muffle is 8·75; but sometimes it amounts to 12 or 16; the manufacture of sulphuric acid from blende, therefore, pays very badly at the low price of pyrites, and the just-mentioned amount of sulphur is, after all, sent into the air as SO_2 and SO_3. He describes unsuccessful efforts at fixing these gases by balls made of common salt (according to Hargreaves), by simultaneous mixture with sulphuretted hydrogen and water, and by the employment of fan-blasts and coke-towers fed with water. In the latter case, at all events, the SO_2 remains mostly behind, and can only be made harmless [?] by dilution with air and very high chimneys. The absorption of the acids succeeded better than by a fan-blast by the employment of a lead-tower of 20 feet diameter and 50 feet high; but even this only condenses a portion of the SO_3, which, as is well known, is difficult to condense in the state of anhydride.

The same drawback, viz. the escape of acid vapours, not specially in the case of blende, but generally in the manufacture of sulphuric and hydrochloric acids, is sought to be avoided by an English patent of Rayner and Crookes (28th July, 1875), which it is best to mention in this place. They propose to conduct the gas through a cylindrical or globular vessel revolving round a hollow axle; by means of the latter absorbents, such as caustic soda, alumina, quicklime, carbonate of soda or of lime, are to be brought into intimate contact with the gas, either in the solid or in the liquid state; the escaping CO_2 can be used for manufacturing bicarbonates. A practical application of this proposal does not appear to have taken place as yet.

All the described apparatus for burning small pyrites depend upon an external source of heat. Whilst the muffles consume ordinary fuel, the other arrangements presuppose the assistance of pyrites in lumps, *at least* of the same weight as that of the dust, mostly more. This evidently does not satisfy all requirements; for there occur enormous masses of pyrites as smalls, either coming from the mines as such, or produced by separation in the wet way, and in some cases, such as zinc blende, the mineral is purposely pulverized, and no pieces at all come in. For these cases, where no lump pyrites could be employed at the same time, previous to Gerstenhöfer's invention only muffle-furnaces could be used, with all their drawbacks. Although this could be done very well in the case of blende and other ores, where the metal was the main thing and the sulphurous acid altogether a secondary matter, it could only be done exceptionally and with great trouble for ores where the sulphur forms the principal valuable portion. The invention of Gerstenhöfer's burner was therefore received with great joy and somewhat too highly strung hopes; and if this burner has not fulfilled all expectations, it has at any rate given an impulse to the construction of apparatus more serviceable for the manufacture of sulphuric acid.

The furnace of Moritz Gerstenhöfer first became publicly known in 1865, although it seems to have been in operation a little earlier. The description and diagrams of it will be reproduced here from Schwarzenberg's treatise, p. 415. Figs. 68 to 71 represent such a furnace on a scale of 1 to 50, viz.:—fig. 68, a vertical section through the lines V V of the plans figs. 70 and 71, along with a front elevation; fig. 69 a vertical section through the line X X of the plans figs. 70 and 71; fig. 70 a sectional plan through the line Y Y of figs. 68 and 69, and, besides, a view from the top; and fig. 71 a sectional plan through the line Z Z in figs. 68 and 69.

The inner shaft of this burner, which is lined with fire-bricks, is 17 feet high, 4 feet 3 in. long, and 2 feet 7½ in. wide inside. It must first be brought to a white heat by putting in a temporary

Fig. 68.

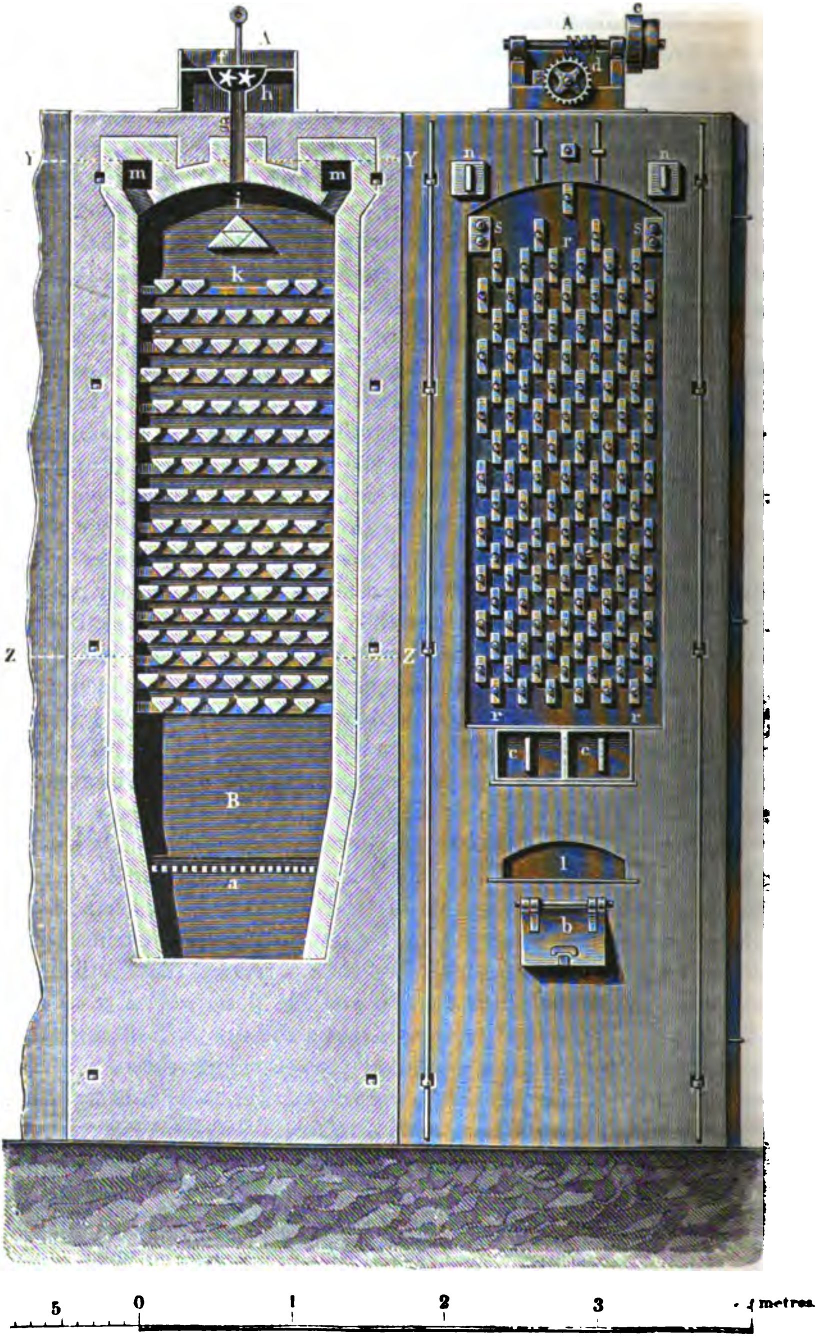


Fig. 69.

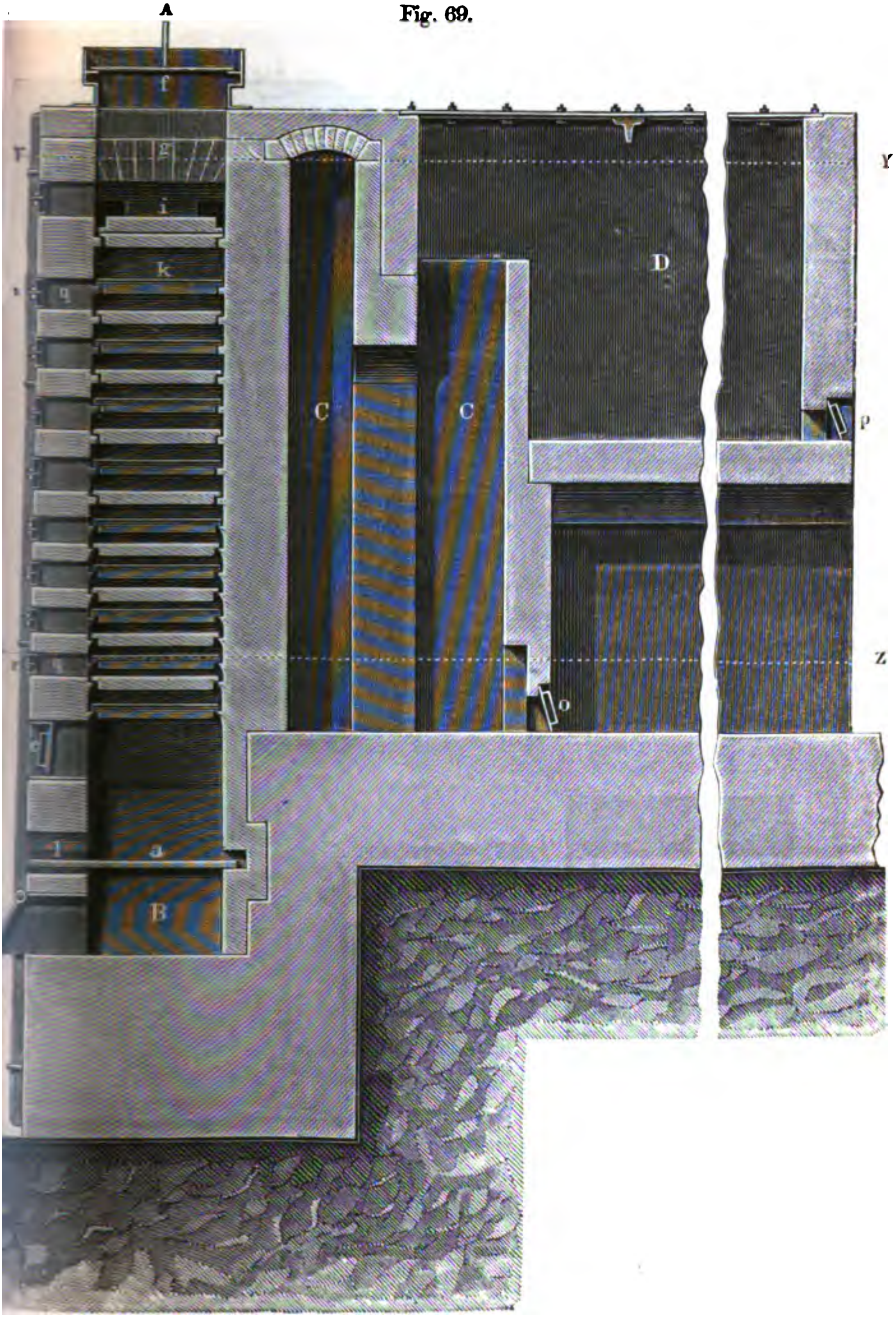
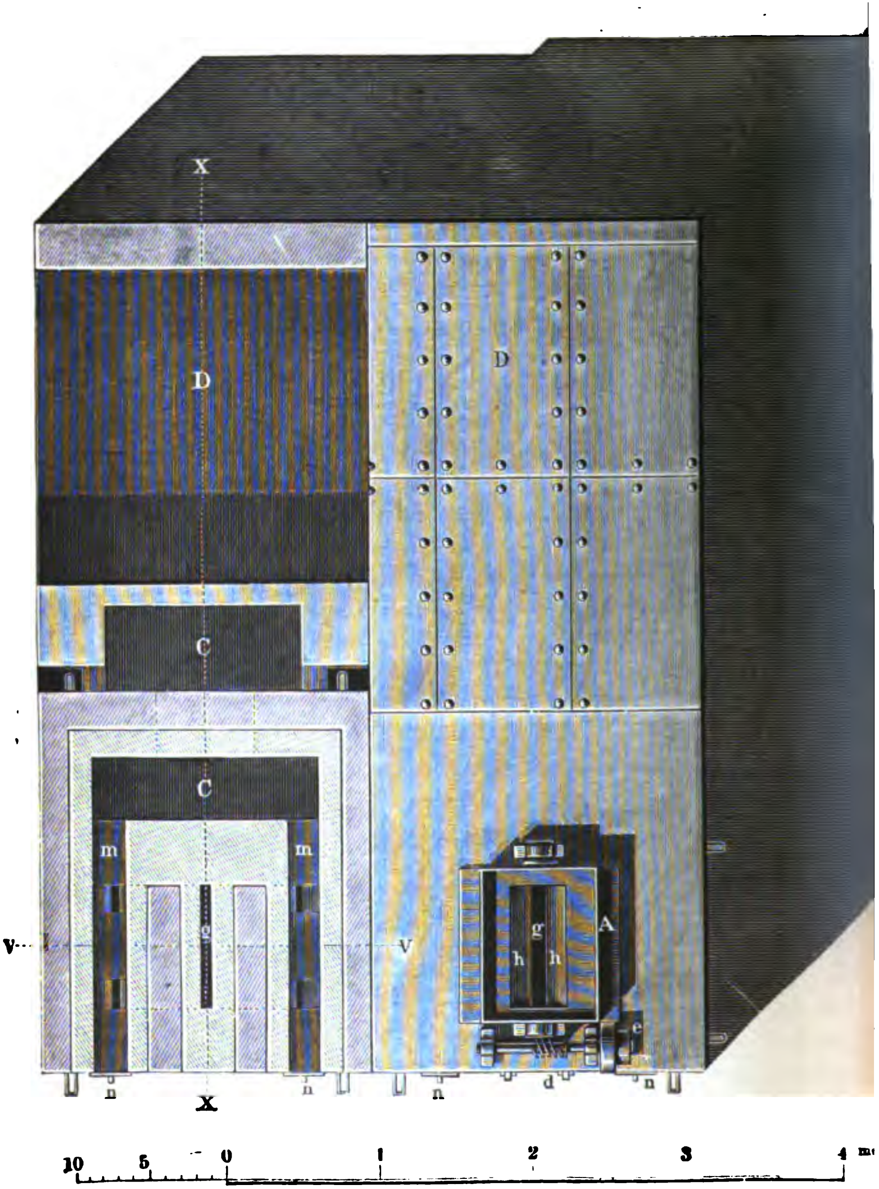
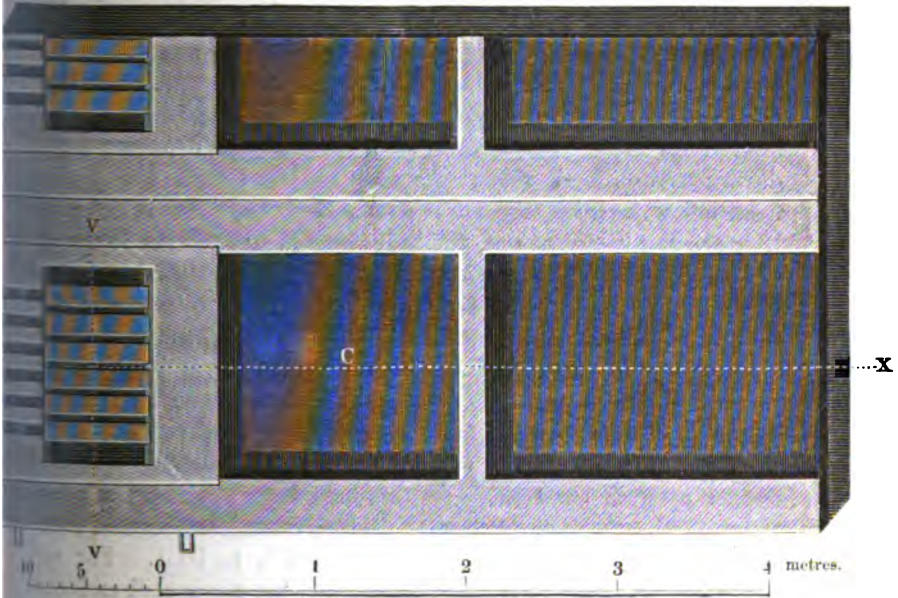


Fig. 70.



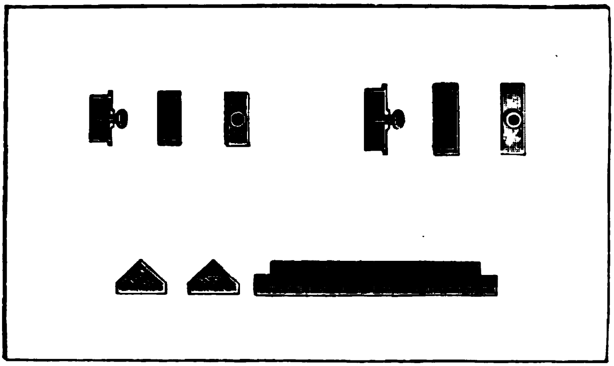
grate *a*, walling up the opening *l*, and lighting a strong fire through the openings *c*; the lower door *b* allows the air to enter. During this time the burner is not connected with the acid-chamber, but by a side flue with the chimney, which draws off the products of combustion. When the furnace has got up to a white heat, the supply of ore is commenced. The ore must be put on as a perfectly dry powder of regular grain, sifted beforehand. It is put into the cast-iron box A, which on the top is continued into a wooden hopper, and which contains the charging arrangement for regulating the supply of ore. This consists of two fluted rollers 3 inches in diameter outside, 2 inches between the flutes, with flutes ⅜ inch wide, turned round their axles in opposite directions by the toothed wheel *d* worked from the pulley *e*. By the speed of these rollers the supply of ore is regulated; in the beginning they are only allowed to revolve once in five minutes, at which rate it takes seven hours to fill the burner. The cover *f*, adjustable to different distances from the rollers, protects them against the pressure of the ore.

Fig. 71.



The rollers allow the ore to fall into the slit *g*, which is luted by the ore lying over the rollers, so that no gas can escape. Through *g* the ore falls upon the fireclay prism *i*, and from this, spread on both sides, onto a series of four prismatic fireclay bars, which divide it again and allow it to drop on a tier of seven similar bars lower down. Fifteen similar tiers follow below these, consisting alternately of six and of seven bars, so disposed that the intervals of each upper tier are covered by the bars of the next lower tier. The ore gradually drops through into the lower part of B, being caught at each passage by a series of bars of the lower tier, and, after it has attained its natural slope on the same, dropping further down again on both sides. As soon as the fourth tier (counted from below) is filled, the fire is drawn from the grate *a*, the grate-bars are singly pulled out, the holes walled up, and the lower part of shaft, serving up to this time as an ash-pit, is cleaned and closed up to the holes required for supplying the necessary air; then the gas is still allowed for a short time to escape through the chimney; at length the connexion with the chimney is shut off completely, and that with the acid-chambers is opened. Formerly, by means of a fan-blast, *hot* air was always supplied; now only *cold* air and natural draught are employed when burning pyrites or copper-pyrites: the reasons for this have been explained in a pamphlet on this furnace by Bode (' Beiträge zur Theorie und Praxis der Schwefelsäurefabrikation,' Berlin, 1872, p. 105). For very badly burning sulphides, such as blende, hot air is still preferred. The ore in dropping down is brought into intimate contact with the air coming from the bottom, and with its increasing oxidation and desulphurization it meets air always richer and richer in oxygen, so that its complete burning is much facilitated. The sulphurous acid, the oxygen in excess, and the nitrogen go from the burner through the flues *m*, provided with cleaning-doors *n*, into the main flue C, and from this through the dust-chamber D towards the acid-chambers. The openings *o* and *p*, usually closed by iron doors, serve for cleaning the main flue and the dust-chamber. The latter is covered with metal plates, on which the ore is dried. The front wall contains, between the tiers of the bars, the openings *q*, closed with iron boshes *r*, which in front have a round hole stopped by an earthenware plug. These serve for observing the ore and for introducing an iron hook when the spaces between the bars have to be cleaned, which is done once every three hours. Also in the upper part of the burner, the flue-dust there collecting must be pushed off now and then by means of the boshes *s* (fig. 68). Fig. 72 shows the details of the boshes and of the fireclay bars. In such a burner 5 tons daily (according to some—only 2 tons according to others) can be burnt; Bode (p. 42) states the proper figure for pyrites as 2½ to 3 tons. In this case the space B must be cleaned out once every six hours; to lessen the entrance of false air, the rake is put in through a small easily closed recess in the movable door *b*. The burner requires the labour of four men, who, however, can serve several burners. The result is principally dependent upon the skill and attention of the man who has to clear the spaces between the fireclay bars. During normal burning the highest temperature, a white heat, is present about the middle of the height; higher up it decreases to a low red heat; the lowest layers of ore are not even red-hot. If too much air gets in, the heat spreads higher up; with too little air it comes lower down; the burner in the former case gets too hot, in the latter too cold. In the former case less air is admitted or more ore is put in by quickening the movement of the charging rollers; if by too hot work fluxing of the ore sets in, the green ore must be mixed with burnt ore till all is put right.

Fig. 72.



Schwarzenberg, as well as Knapp ('Chem. Technologie,' i. 2, p. 314), very highly commend this burner for metallurgical operations, but doubt its usefulness in the manufacture of vitriol,

Fig. 73.

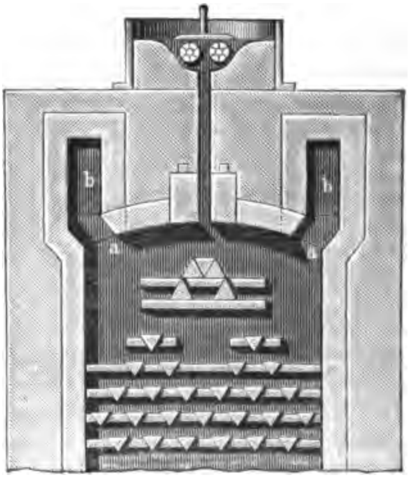
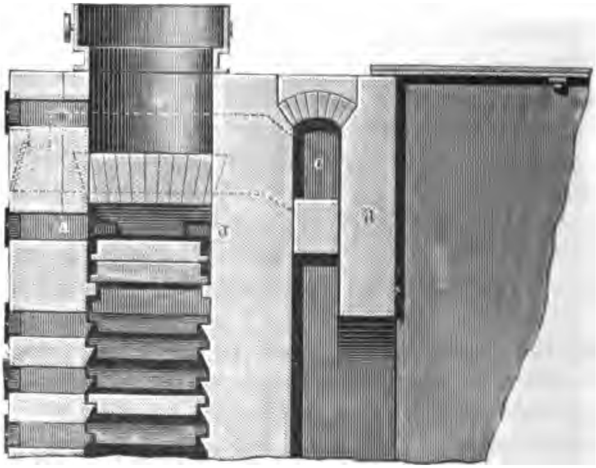
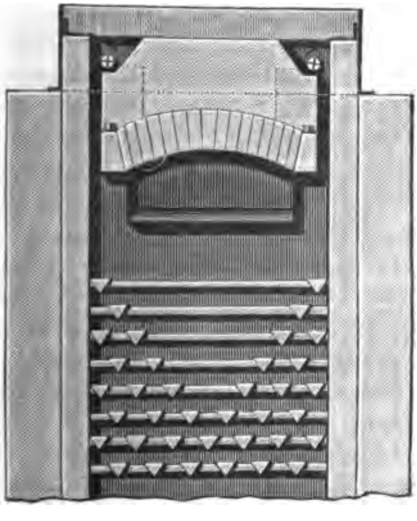


Fig. 74.



both on account of the large quantity of flue-dust and of the liability to fracture of the fireclay prisms. Bode contests these objections, but admits others. According to him, the heat need not exceed a red heat; the clay prisms, if made of good material, stand very well; if one or two are broken, it does not matter much; and they can easily be removed and replaced. The flue-dust is more considerable than in muffles, but, when the work is most hardly driven, only amounts to 7 per cent., otherwise only to 5 per cent. The construction has therefore been simplified, as shown in figs. 73 and 74. *a a* are lateral openings in the arch, connected with the side flues *b b*; the latter are connected backwards with the flue-dust chamber at *c*; but they first meet the brick curtain *d*, by which the current of gas is deflected downwards, and thus the deposition of the dust is assisted. The flues *b b* are continued towards the front, and closed by a plate; if the flues are to be cleared, the plate is removed and the deposit pushed, by means of a rake, partly into the furnace-shaft, through *a*, and partly into the chamber, through *c*, which can be done in a few minutes. If 2 tons are burnt in twenty-four hours, this need only be done once a week. A further contrivance for lessening the quantity of dust is shown

Fig. 75.



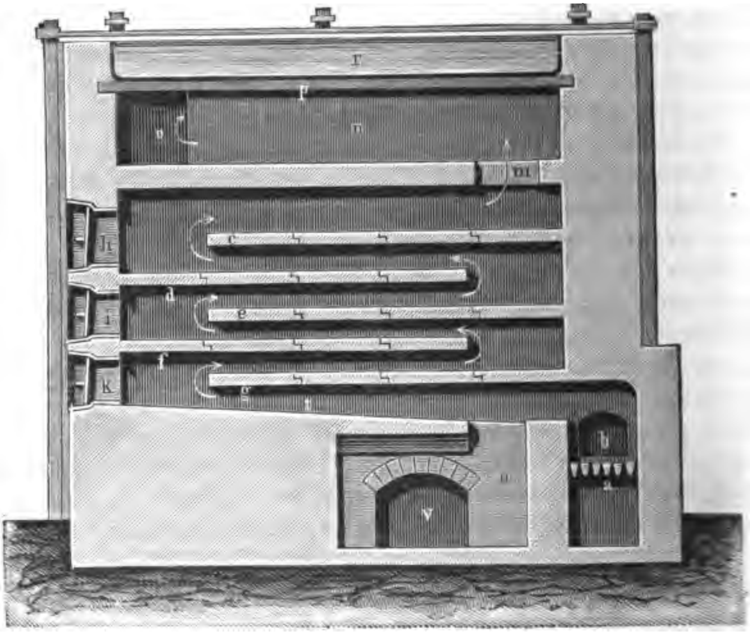
in fig. 75, from which it is seen that the ore drops down in two jets, but not immediately in front of the opening for the escaping gas. Bode further describes some improvements in drawing out the burnt ore, with the view of restricting the rushing-in of false air to a minimum. He also contradicts the assertion that the flue-dust chamber is acted upon by the hot acid vapours. In his pamphlet, Bode specially notices the objection urged against the Gerstenhöfer burner, that it does not permit complete desulphurization. Galena certainly cannot be treated in it, any more than in any other apparatus, so as to obtain sulphurous acid from it, for reasons mentioned before. Blende, however, if finely ground, can be got down to 5 or 6 per cent. sulphur, which certainly necessitates further calcining in an open roaster, but still pays for making sulphuric acid (p. 112). "Coarse metal" with 25 to 29 per cent. sulphur, 12 to 14 per cent. of which should be removed, is easily treated in this burner, and yields gas of 6 per cent. SO_2. Iron monosulphide, which is obtained at Freiberg as residue from sublimating arsenical sulphuret, can only be used if mixed with smalls from rich pyrites. Pyrites, according to Bode, gives richer gas and better-desulphurized cinders (2·75 to 5 per cent.) than the same ore in pieces in the ordinary burners. In this case, however, the general practice contradicts Bode; for bad desulphurization has been the cause of Gerstenhöfer's burners being done away with again in several places. Thus at Messrs. Muspratt's works at Widnes and Flint, the ore, after once passing through the burner, still contained 12 per cent. sulphur. It appears that now this burner is only used for metallurgical purposes, where the sulphurous acid is merely a secondary consideration. For poor ores especially it is useful, and furnishes strong gas available for sulphuric-acid making. Where complete desulphurization is not required, it still seems the best of all apparatus, and is, for instance, still used at Freiberg for the preliminary roasting of mixed ores. For rich pyrites, however, it has not been able to make its way, and has been abolished again at Chauny, Widnes, Nienburg, Stolberg, and other places. Out of Germany it appears to be at work exclusively at Swansea, for roasting coarse metal in copper-smelting.

The question whether this burner is well adapted for ores and metallurgical products inclined to flux, is mostly answered in the affirmative; the question respecting flue-dust is mostly decided against it. A drawback of Gerstenhöfer's burners not to be overlooked is this, that they only work well with ore of equal grain. The expense and trouble of attaining this have contributed to their rejection in English works. Bode himself (Dingl. Journ. ccxii. p. 58) states that the grain ought not to exceed 1 millim. ($\frac{1}{25}$ inch); otherwise very much sulphur remains in the cinders. This condition, very difficult to realize on a large scale, probably explains the unsatisfactory results in England. Whether, as asserted there, more nitre is consumed with them than with other contrivances for burning smalls is not quite clear.

Whilst the ingenious and original invention of Gerstenhöfer has not fulfilled the hopes which it had raised, at any rate for the manufacture of sulphuric acid, another, extremely simple invention has been crowned with very great success. Juhel, the manager of Malétra's works at Rouen (the author has heard this name stated as Jouelle), had the idea of cutting the Olivier-Perret furnace (which is inconvenient to attend to and requires as much lump ore as smalls) in two—that is, of burning the lumps by themselves and mounting the plates for the smalls separately. He thus applies the same principle which Gerstenhöfer had employed, and the mathematical proof of which had been given by Bode in his 'Beiträge,' viz. that, for the small ore as well, its own heat of combustion is quite sufficient when once the process has been started. Malétra's burner, as it is generally called (although Malétra himself was not the inventor), is, so to say, the egg of Columbus. This burner, the simplest and cheapest of all dust-burners, has become comparatively slowly known; but since 1873, when it became better known by the Vienna Exhibition, it has spread on the Continent with extraordinary rapidity, whilst it has attracted little attention in England. The first burner out of France seems to have been erected at the works of Schnorf Brothers, at Uetikon, near Zürich, in 1870; in Germany the first was erected at Kunheim's works in Berlin. Even if, as it would seem, some form of these simple shelf burners had been previously in use here and there, their *successful* application for burning pyrites smalls seems first to have been effected by Malétra's works.

Fig. 76 gives a longitudinal, fig. 77 a cross section, the latter through two furnaces. Usually a whole set is built in a row. In order to start it, a coal-grate, *a*, and fire-door, *b*, are provided, which are walled up when the burner has got up to a white heat. During this time the top working-door remains open. Then the five plates *c, d, e, f, g* are charged with small ore through the doors ***h, i, k,*** whereupon the pyrites takes fire at once. The air enters through *l,* and is regulated at will. The gas travels over all the plates in a serpentine line, indicated by the arrows, escapes through *m* into the dust-chamber, *n,* and through *o* into the acid-chamber, or into another dust-chamber. The chamber *n* is covered by a metal plate, *p,* upon which lead pans, *r, r,* are placed, in which all the chamber-acid can be concentrated from 112° to 144° Tw. The acid of one pan communicates with that of another (as usual) by siphons or by simple run-overs. Each of the shelves, which are 8 feet long and 5 feet wide, consists of eight plates in two rows of four each; they rest, at the sides, in the walls of the burner, in the middle on fireclay bearers, *s, s,* whose shape is better shown in fig. 78. They are not equidistant, as can be seen in the drawing; the upper shelves, where more gas is evolved, are more widely apart

Fig. 76.



than the lower ones, where the radiant heat of the shelves is all the more useful. The best distance for the upper shelves is 4½ inches.

Fig. 77.

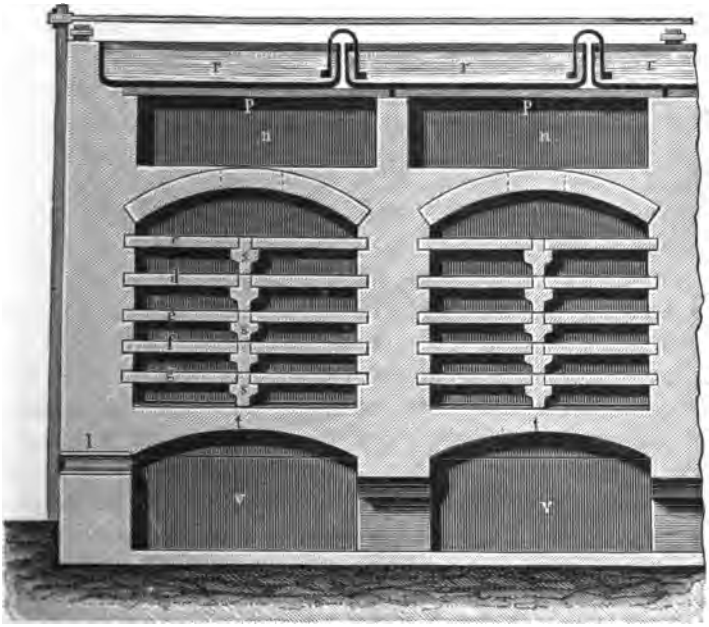
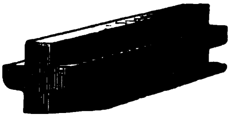


Fig. 78.

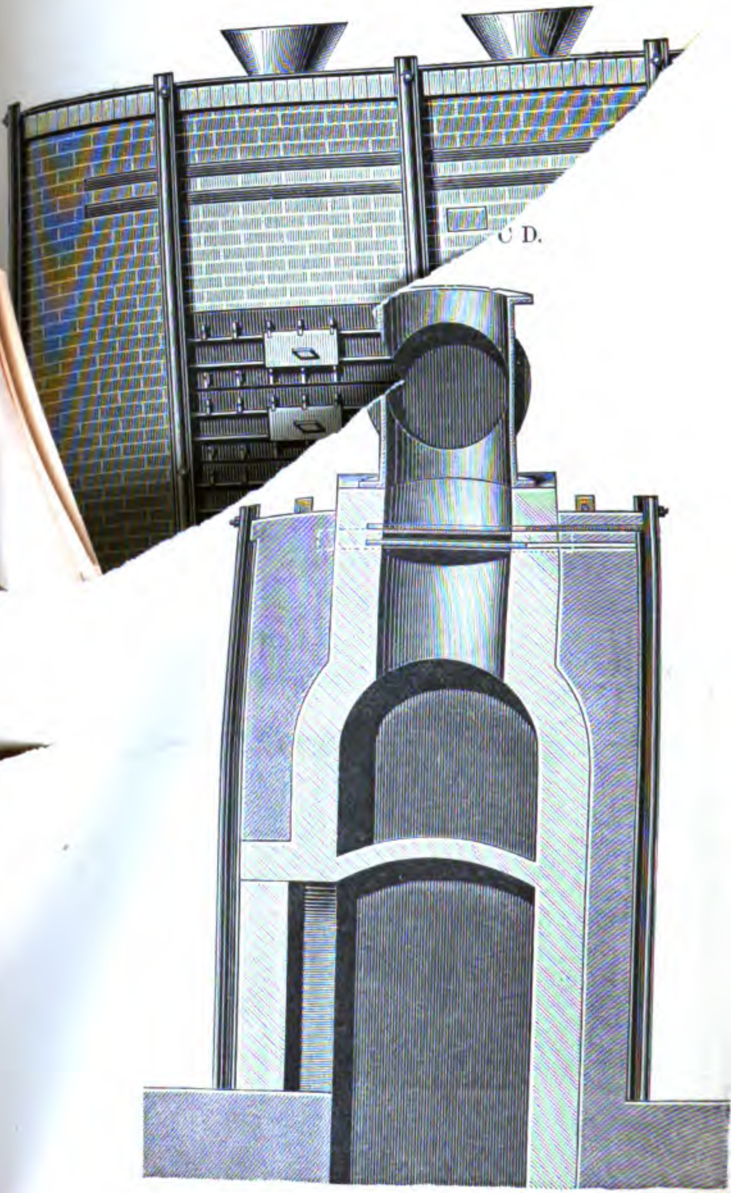


In order to burn a larger quantity of pyrites, it is not possible to leave the ore lying quietly, as in Olivier-Perret's burner: since here the external heating by the lump ore is missing, the combustion would be too incomplete, and the heat would soon get so low that the burning would cease. The mass must therefore be moved, which is done in the following way:—Every four hours the contents of the lowest plate, *g*, are drawn through the door *k* onto the arch *t* (which is level at the top, but slopes behind), after the burnt ore lying on the same has first been pushed through the same door *k*, to the opening into the pit *u*. Then, through the door *i*, the contents of *f* are pushed down to the plate *g*, and there levelled again. Thus the higher plates are successively treated, till the highest plate, *c*, is emptied, and can be charged with fresh ore. If four furnaces go together, one of them is on turn every hour. The contents of the pit *u* are removed once a day by the door *v*. The movement of the ore by removal from one shelf to another causes its thorough combustion, and thus also raises the heat. Four furnaces of the above dimensions burn daily 3 tons of pyrites. From 6½ to 7 lb. of ore are calculated for each superficial foot of shelving.

The burning in Malétra's burners is excellent. At Uetikon 48-per-cent. Lyons pyrites is regularly burnt down to 1 per cent., at most 1½ per cent., of sulphur—that is, better than in any of the burners hitherto mentioned. At Kunheim's works the figures are 1·45 to 1·9 per cent. sulphur. It is doubtful whether the shelf burner answers as well for poor ores as for rich ones; probably for the former Gerstenhöfer's is preferable. But the shelf burner has one drawback: the frequent opening of the doors for pushing on the ore requires much labour, and allows much false air to get in, with its attendant effects on chamber-space, yield of vitriol, and consumption of nitre. Possibly the mechanical furnaces next to be described would remedy this drawback; but they must necessarily increase another drawback mentioned in connexion with the shelf burner, viz. flue-dust. In the case of MacDougall's burner this has actually prevented its employment in certain cases. To be sure, Bode (Dingl. Journ. ccxxv. p. 279) has found the gas from the shelf burners very rich indeed, viz. (in the case of one just started, and served by unskilled men) ranging from 6 to 8·20 per cent. SO_2—that is, just as good as from ordinary lump-burners. Bode has never noticed any scarring, and has found that more sulphur can be left in the cinders, if this is desirable, for further metallurgical operations. All the statements received by the author (from a number of works) agree in this, that the yield and the consumption of nitre at works using the shelf burners are at least as favourable as in any other works where nothing but pieces are used.

Malétra's burner, which has now obtained general acceptance in Germany, has been improved by Schaffner, P. W. Hofmann, Bode, and others. Kunheim charges both sides together; so that the time during which the doors are open is much shortened. The burner allows the use of pieces up to ¾ of an inch in diameter. Two men per shift usually serve from one to four burners. One man attends upon four of Bode's burners, consuming 3 tons of ore in 24 hours, and at the same time gets out the burnt ore. For wheeling this

To face page 219.]



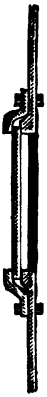
C D.

E

away one man is occupied for three hours every other shift. Bode's patent circular set of burners seems to be a particularly rational arrangement.

The shelf burner constructed by Mr. Schaffner, of Aussig, through whose kindness I am enabled to give detailed drawings of the same, is considered one of the best modifications of this apparatus. It is shown in figs. 79 to 83. It has seven plates, each served through its own door—three on one side, four on the other. On the first side there is also the ash-pit door, 18 inches square, for drawing out the cinders, which is thus done in the usual way, not by the rather inaccessible pit of Malétra. The doors all slide with their planed margins on equally planed ledges cast on the front plates; so that luting or plastering is not necessary. A certain number of angle-pieces are bolted to the front plates; these, between their outer bend and the planed ledges, leave sufficient room for the doors to slide each way; and there is a sufficient number of such pieces present for each door to be always held by three of them (fig. 84). This style of work is evidently much cheaper than casting every thing in a piece, because the planing is much easier; it is also cheaper than the English style, shown on p. 171, and quite as substantial as the latter. There are no special openings for the air, as, in spite of the planed surfaces, sufficient air enters to support the combustion. The regulation of the draught is here effected entirely by the chimney-damper.

Fig.84.



The shelves are made from excellent fireclay slabs, manufactured at the Aussig works themselves. They are 5 feet long (equal to the width of the burner *plus* the bearing on each side) and 18 inches wide. They run from side to side without any middle bearings, their lower surface being formed in the shape of an arch; so that they are about 3½ inches thick in the middle and 6 inches thick at the ends.

The whole set is covered by a flue-dust chamber, continued into a larger chamber behind, from which the gas during the heating-up goes by an underground flue to the chimney, and during the work itself by a metal pipe to the Glover tower. Through the upper dust-chamber a charging-hopper passes for each burner. The tubular part of the hopper is closed by a small cast-iron cone with its base downwards, which is continued upwards into a rod projecting out of the hopper, and connected with a horizontal lever, whose outer arm has a balance-weight attached to it. By means of this the hopper filled with small ore can be emptied easily and instantaneously by pressing down the outer arm of the lever. The cone then goes down again, and the joint is made gas-tight by putting a new charge into the hopper. In this burner *dust and peas* are burnt *together*, and the sulphur burnt down to 1 per cent.; thus the grinding of the smalls, which is still practised at some works, is saved.

Analogous to Malétra's burner, which applies the Olivier-Perret principle for the *independent* burning of smalls, is the *new* furnace of Hasenclever and Helbig (Dingl. Journ. ccxxii. p. 250), which is an essential modification of their former burner, and was to permit the combustion of small ore without the assistance of lumps.

Figs. 85 to 89 give separate sections of the burner. The ore is charged into the funnels, a_1 to a_5, and covers all the plates in the shaft down to $h_1, \ldots h_5$. As burnt ore is taken away below, fresh smalls slide after from the funnels, a to a_5, exactly as in the former burner of the same inventors. To be sure, in that case floury ores would not slide down very well, as will be remembered. The air enters at b, and, in the direction shown by the arrows, ascends over the ore on the four or five lowest tiers, cools this, and is heated itself. At c the air, mixed with a little SO_2, leaves the burner, and enters again at d more highly heated, descends along the ore, and, when hottest, comes into contact with the nearly burnt-off ore, so that complete desulphurization can take place. The hot gas leaves the burner at c, and through two shafts, connected by pipes, gets to f, towards the acid-chambers, whilst the air serving to maintain the combustion heats itself on its way from c to d in contact with the brickwork heated by the gas. Bode points out that in Gerstenhöfer's burner the heating of the air had been prescribed as well, but had been given up as too troublesome. The author is afraid that any complication in the way of leading the gas in the burners would cause serious difficulties concerning the draught. If the gas is to go downwards again, this will frequently lead to its blowing out, to insufficient heat, and bad burning. The gas ought always to be taken away in the simplest possible manner, so that it will always travel upwards. Even if this objection against the Hasenclever-Helbig burner were removed, there would be still a danger of the spaces between the

Fig. 85.

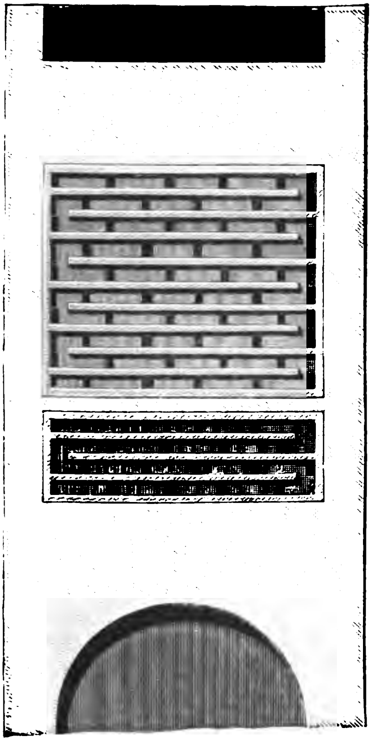
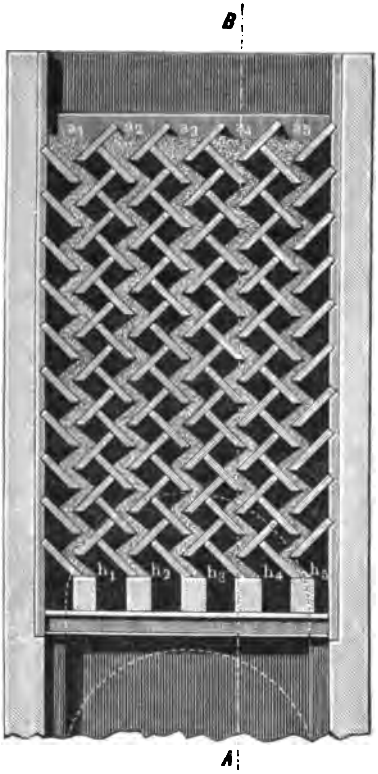
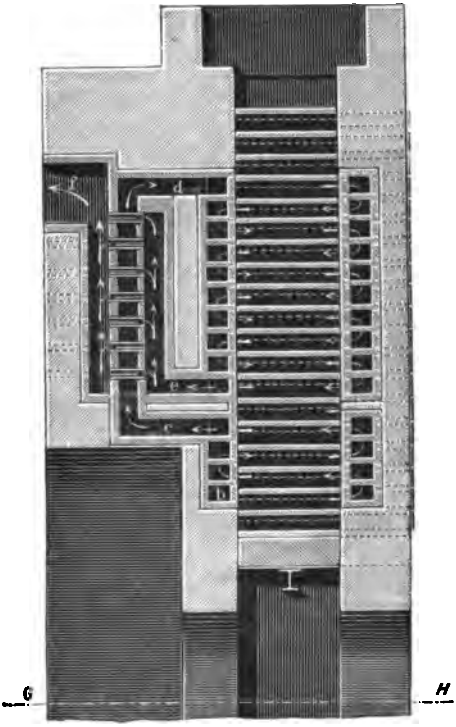


Fig. 86.



plates, which are very badly accessible, getting stopped and scarred up. It is not very clear what advantage is to be derived in comparison with the simple shelf burner, except the automatic movement of the smalls, which, however, will hardly proced smoothly without manual labour to help it on. The inventors themselves have therefore not carried out that construction in practice (Dingl. Journ. ccxxvii. p. 71).

Fig. 87.



Theoretically, probably the most perfect of all the dust-burners is that of MacDougall Brothers, patented a few years ago, of which drawings are given in figs. 90 to 92. The burner consists of a metal cylinder, 6 feet in diameter and 12 feet high, formed of seven rings (*a a*) bolted together, and provided with a solid bottom, but open at the top. The rings are cast in such a way that the lower and inner edge of each can serve as an abutment for one of the flat arches b_1 to b_6, which divide the inner space of the cylinder into seven chambers, the uppermost of which is open at the top. The arches, as well as the cast-metal bottom of the cylinder, are pierced in the centre, and allow the passage of a cast-iron shaft, *c*, 6 inches thick, which is turned by means of the toothed wheel *d*, the pulley *e*, and the steam-engine, *f*. The shaft carries at top and bottom the lutes *g* and g_1, into which the cups *h* and h_1, fixed to the top

Fig. 88.

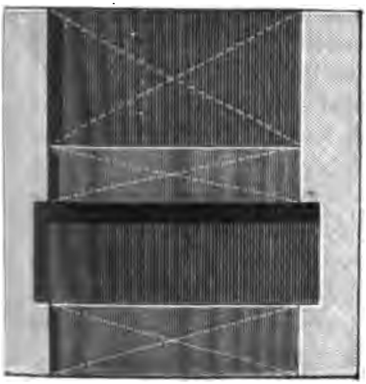
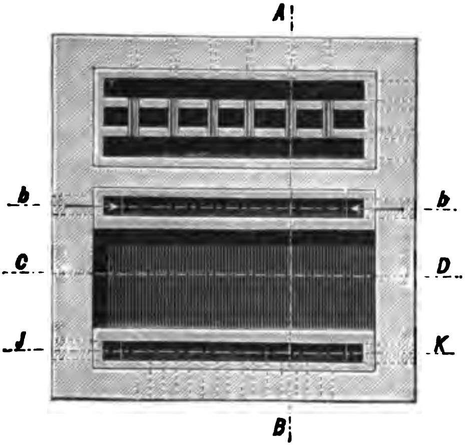


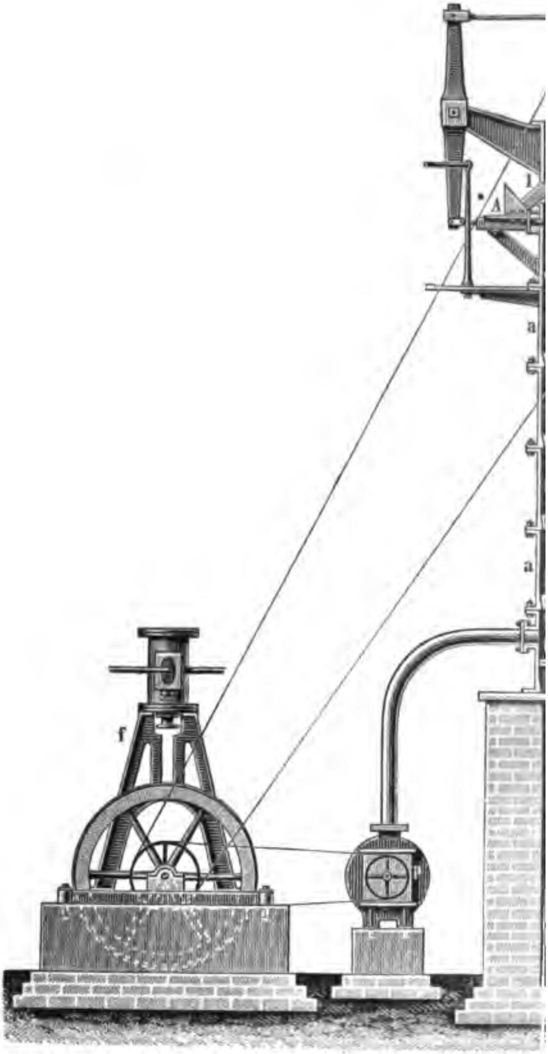
Fig. 89.



arch and the cylinder-bottom, enter; the latter are fast, whilst the lutes *g* and g_1 turn round with the shaft, and a hydraulic joint prevents the escape of gas at the places where the shaft enters and leaves the cylinder. To the shaft are fixed the cast-iron arms, $i_1, i_2 \ldots i_7$, provided with teeth along their lower margin. The teeth are placed alternately in opposite directions; so that the arm i_1 moves the ore-dust from the centre to the periphery, i_2 the same from the periphery to the centre; i_3 acts like i_1; i_4 like i_2, and so forth. Corresponding to this, the arches are perforated alternately—b_1, b_3, and b_5 near the margin, b_2, b_4, and b_6 in the centre. The latter have a large central opening, 1 foot 3 inches wide, lined with a metal pipe, which gives free play round the shaft to the gas and the ore-dust; whilst in the other arches the shaft is so tightly surrounded by a metal pipe, that scarcely any dust, and still less gas, can get through. The small ore (which need only be passed through a 1-inch riddle, and therefore contains pieces up to the size of a walnut) is lifted by the elevator *k* (also moved by the engine *f*), and is emptied onto the top flat, b_1, where the arm i_1 takes it round and gradually moves it towards the periphery. During this time the ore is completely dried by the heat of the gas below. The ore dropping down the edge at *l* from the open top chamber is continually pushed into the first closed chamber by a ram at A. The ram A can be moved reciprocally either by rod B or C, and can be moved more or less quickly; so that feed of ore can be regulated to a nicety. The arm i_2 moves th towards the centre of b_2, where it drops down; i_3 moves it tow the periphery of b_3, where it drops down again, and thus quite gr ally and constantly, being directed by the teeth of the arms, a at the bottom, and is emptied out through the pipe *m*. Th slides, *n* and *o*, allow the contents of *m* to be got out withou loss of gas or any air entering the other way. As the fu during the operation is in full heat, most of all near the to ore ignites as soon as it arrives on the bottom of the first chamber, b_2; and in its gradual zigzag way towards the b the sulphur is completely burnt off. The air is continually su by the air-pump *p* in exactly the necessary quantity; and t escapes through the pipe *r* to the acid-chambers.

An apparatus such as is here figured is sufficient for b 3½ tons of ore in 24 hours; with eight closed chambers, inst six, it can burn 5 tons. It is also very well adapted for burni spent oxides of gas-works; but then it must have only four bers. In a factory on the Tyne, where this apparatus was at w a time, the consumption of coals for driving the engine amoun 4 tons per week. A two-horse-power engine and a 1½-inch pipe are said to suffice for the largest burner. The wages amo to £4 5*s*. per week; but this rather high amount was explai the fact that two other furnaces were building, which were ex to be served by the same men who attended the first. Of this apparatus is quite independent of the skill of the burner which is mostly only acquired by some years' practice.

For heating up, the engine is started, and the cold furn gradually filled, care being taken to regulate the thickn the layers of ore on the different floors. When the ore h rived at the bottom, the engine is stopped, and the flam temporary fireplace, built against the cylinder, is allowed to it, until the ore lying on the bottom and the floor b_2 has fire. Then the engine is started, the temporary fire-place is away, the man-hole is closed, and nothing remains but to se the ore arrives at the bottom properly burnt. If this s not be the case, the speed of the feeding-ram A, that of th pump, or that of the agitating-shaft is altered till every thing order. It is easy to get the sulphur in the burnt ore


l
A
a
a
f

to 1 per cent.; in forced work only 3 to 4 per cent. can be attained.

One objection will at once be made to MacDougall's burner, viz. that the machinery in its interior must wear out very quickly. In order to obviate this, all parts of the machinery are made of thick cast-iron; and when one of the arms is worn out, it can be renewed through the man-holes, *s s*, without allowing the apparatus to cool down. That otherwise this burner has many very great advantages over all others is evident. The turning of the small ore is perfect without any opening of the doors and working by hand. Not even during charging and discharging does false air enter the burner; and by means of the air-pump exactly the necessary quantity of air can be admitted (this, however, in practice was found to be very difficult). The work, indeed, is done under such favourable conditions as are realized by no other burner, whether for pieces or for smalls; and it might be assumed that the consumption of nitre would thus be reduced to a minimum, and the yield of acid raised to a maximum. Nevertheless MacDougall's burner had to be given up again in the above-mentioned factory, because the quantity of flue-dust was so great that it could not be managed in any way, and the chamber-process was seriously interfered with. Employment of the Glover tower was not to be thought of. It does not appear that really efficient dust-chambers were employed. The air-pump acted so violently that the dust was carried away a great distance. Probably this drawback might have been counteracted by some alteration in the construction; but, altogether, the machinery caused endless trouble, continually requiring repairs, and there is no doubt that it would have to be altered a good deal before it could become a real success.

A similar furnace was patented to Michel Perret, in France, on June 23rd, 1875. Those who are interested in mechanical calcining furnaces generally will find this subject treated at length by Bode in 'Dingler's Journal,' ccxix. p. 53, and Wagner's 'Jahresbericht,' 1876, p. 298.

We will conclude this long chapter on pyrites-burners with the description of the burner constructed by K. Walter for the special purpose of burning so-called "peas"—that is, small pieces of ore not above the size of a hazel-nut, and not so small as to pass through a sieve with eight holes to the lineal inch. This apparatus is, properly speaking, a modified Belgian burner for lump-ore, similar to those in connexion with Hasenclever's tower (fig. 61). But the figures 93 to 95 show the essential modifications enabling it to do its special work.

Fig. 93.

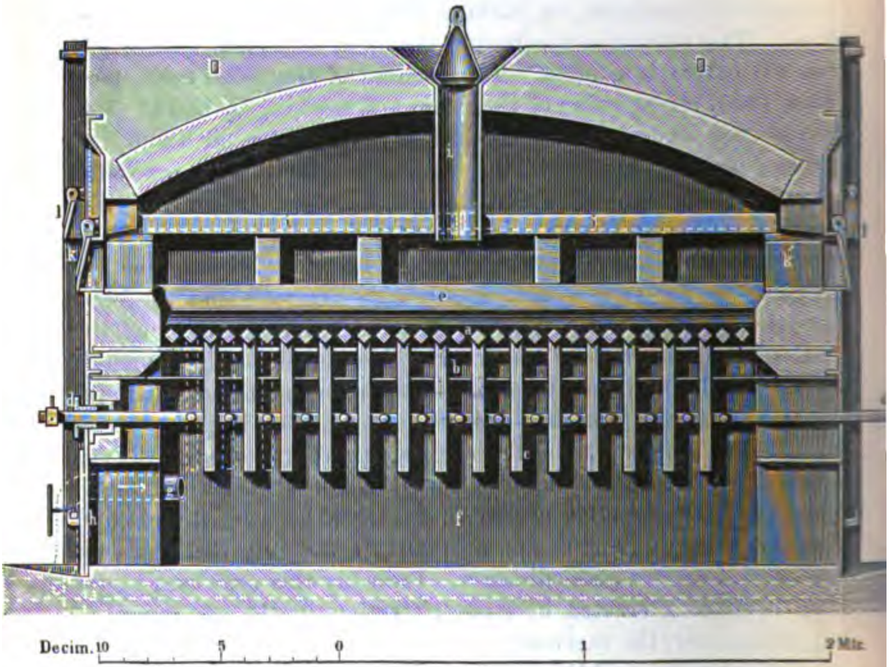
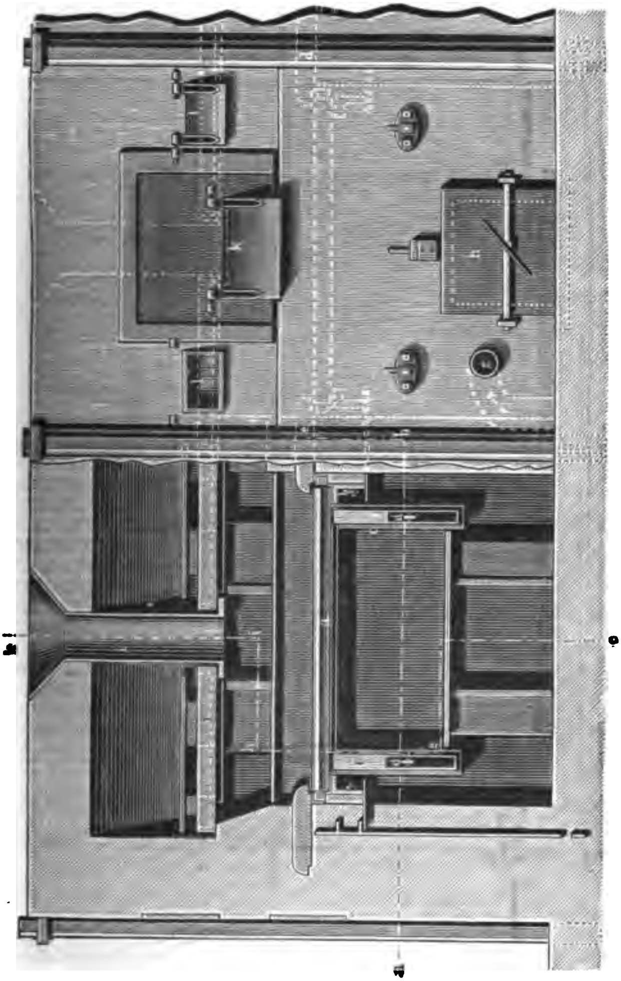


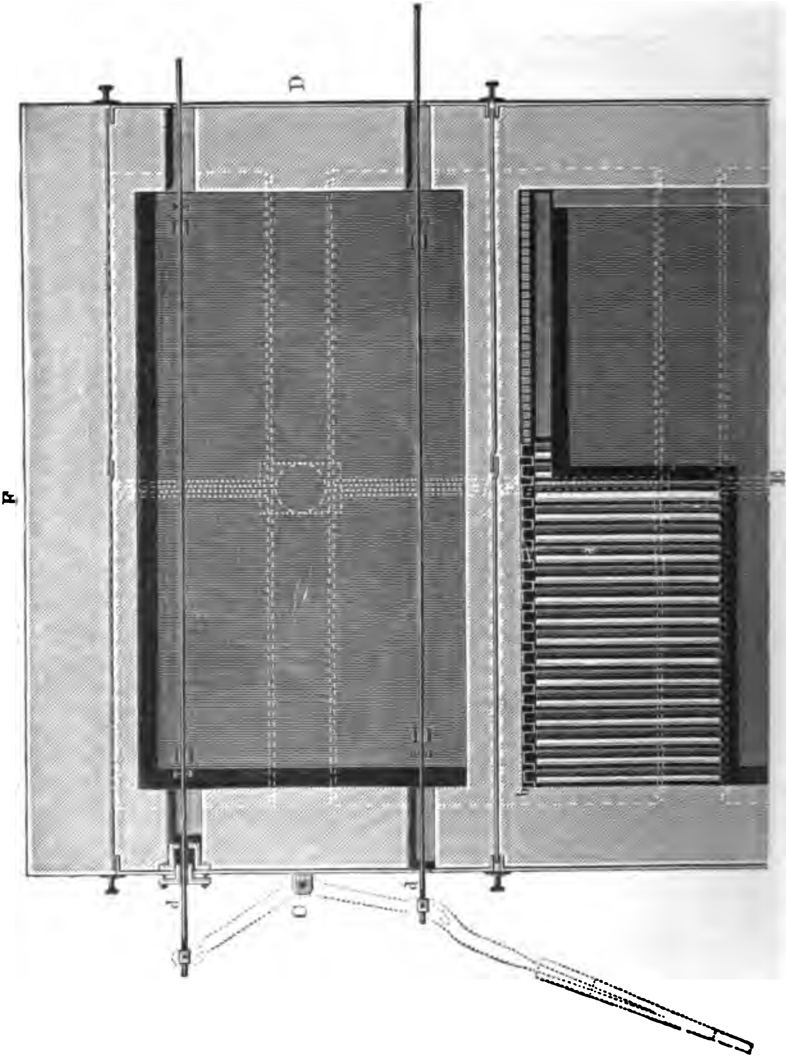
Fig. 93 shows a sectional elevation, taken through the line C D of the plan fig. 95, which itself is taken on the line *a b* of fig. 94; fig. 94 is a section through the line E F of the plan fig. 95, together with a front elevation. There is always a set of such burners built (at least three, at most nine), with a common gas-space, similar to Hasenclever's. The speciality of Walter's burner is this:—the cast-iron grate-bars, *a*, are not, as usual, laid from front to back, but sideways across the burner; they rest on bearings, *b*, and are cast with long projections beneath, *c*, through which a bar, *d*, passes and in front is continued to the outside of the burner through a bosh. The projections, *c*, are not all in the same place, but alternately on the right side and on the left; so that there are *two* bars projecting in front. In each projection, *c*, the bar *d* is provided with a pin which plays in a corresponding slot of the pro-

Fig. 84.



jection *c*; thus, whenever the bar *d* is pulled forward, all the projections are moved with it, and the grate-bars, being cast in one piece with them, are rotated about their axes. According to whether only one of the bars, or, by means of a double key, both of them at a time are moved forwards or backwards, half or all of the grate-bars are rotated *simultaneously*. Since all the parts are fitted very

Fig. 95.



accurately, and afterwards are always moved simultaneously, the distances between the grate-bars can be made very small (say

$\frac{1}{12}$ inch) and continuously remain so. Only this, combined with a very shallow layer of the pyrites, *e* (not above 6 inches), permits the burning of peas. The ash-pit *f* is usually closed, and the door *h* is only opened for wheeling out the cinders; *g* serves for admitting air. The furnace is charged all at once by the hopper, *i*, with a double-conical stopper; and the charge is quickly spread from the doors *k k*. The cinders are let down in a minute by pushing the lever backwards and forwards a few times, the grates just remaining covered by a layer of hot cinders; these, the heat of the brickwork, and also especially the fire of the other burners (a common gas-space is therefore indispensable in this case) almost at once ignite the fresh pyrites. Each compartment, with a grate-surface of 32 square feet, burns from 14 to 20 cwt. in 24 hours. By putting in metal plates, *i i*, accessible through the doors *l l*, some fine dust can be burnt as well; but in the author's experience this burning was very incomplete. Behind the set there is always a chamber for flue-dust; from this the gas may pass into a Glover tower.

Walter's burners, under favourable circumstances, burn the ore down to 3½ per cent. They are at work in several places, and have a good reputation. But they require a strong draught, and cannot easily be combined with ordinary lump-burners to form a set, because the latter, in spite of their ore lying four or five times as deep, at once deprive them of all draught. This might, with sufficient draught at the far end, be managed by very careful regulation of dampers; but in practice it has answered much better to work a set of chambers separately by Walter's burners. When these are short of draught, at once scars are formed, as in the lump-burners. The scars take a flat shape, lying on the top of the ore or just over the grates, and completely stopping combustion there. It is true they are easily broken up and removed by the working-doors; but no proper burning can be expected when they appear in quantity.

Burners for the Spent Oxides of Gas-works.

The burner proposed by Hills has the construction shown in fig. 96, and is so similar to Malétra's shelf burner that no further explanation seems necessary. Quite analogous with this, MacDougall's burner has also been employed for this purpose. A third burner, that of Cowen, is shown in figs. 97 and 98. It consists of a row of fireclay gas-retorts, and requires no further explanation. Other works are said to burn that material in burners with very narrowly-placed grate-bars.

Fig. 96.

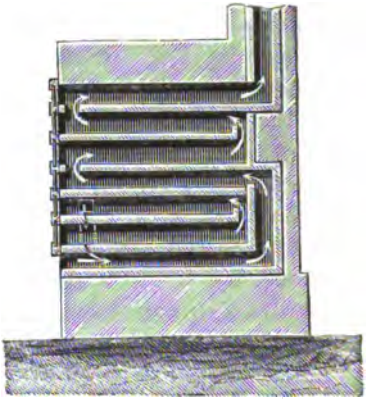


Fig. 97.

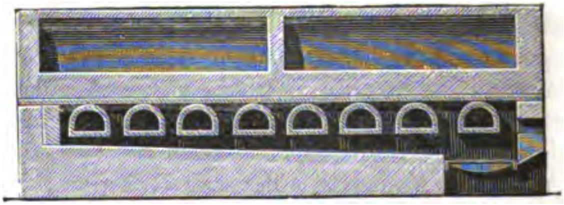
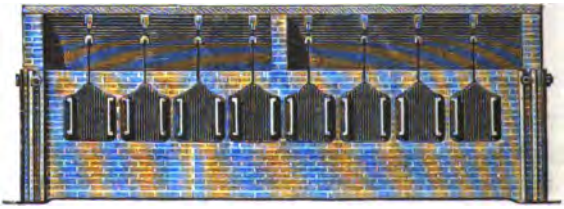


Fig. 98.



CHAPTER VII.

THE BURNER-GAS.

THE *composition of the gas generated in the burners* has been accurately calculated by Schwarzenberg, both for brimstone and for pyrites; and we shall in the first place give his calculations, in which at the same time the *draught* is taken into account, such as is required in normal circumstances.

1. *Composition of the Burner-gas, Draught, and Quantity of Air necessary in burning Brimstone.*

The draught by which air is introduced into the burners, and by which the mixture of gases formed therein, and ultimately that remaining after the formation of sulphuric acid, is carried through the lead chambers and out of them, is of very great importance for the way in which the process goes on.

The draught is generated by several causes, of which the first is the heat of the gaseous mixture contained in the vertical tube leading from the sulphur-burner to the lead chambers. As the density of it is twice as great as that of atmospheric air, it might be supposed that the gaseous mixture formed in the burner was not lighter than the air. We shall therefore compute its specific gravity. As constants for this and the following calculations we shall use the following figures:—

At 0° C. and 760 millims. mercurial pressure

	gram.
1 litre of dry atmospheric air weighs...	1·2932
1 „ „ oxygen	1·4298
1 „ „ nitrogen....................	1·2562
1 „ „ sulphur dioxide............	2·8731
1 „ aqueous vapour	0·804343

Now 1 vol. oxygen gas, on combining with sulphur, forms 1 vol. SO_2, which further requires $\frac{1}{2}$ vol. of oxygen to form SO_3. For each 14 vols. SO_2, containing 14 vols. O, another 7 vols. O are thus necessary for the transformation into SO_3. All this oxygen is introduced into the burner as atmospheric air, containing in 100 vols. 21 vols. oxygen and 79 vols. nitrogen. The above 14+7=21 vols. O therefore introduce 79 vols. of nitrogen into the burner, and the gaseous mixture there formed thus theoretically ought to contain

$$\begin{array}{rll} 14 & \text{vols.} & SO_2 \\ 7 & ,, & O \\ 79 & ,, & N \\ \hline 100 & & \end{array}$$

Experience, however, has taught that for a good working process a further excess of oxygen is required, in the case of brimstone amounting to 5 vols. upon 95 vols. of the nitrogen entering and again leaving the chambers.

If we call the unknown volume of this excess oxygen $=x$, it must carry along $\frac{79}{21}x$ vols. N. To this are added 79 vols. N, entering along with the 21 vols. O required for forming 14 vols. of SO_2 and converting them into SO_3. The volume of the total N and of the excess oxygen required in practice for each 14 vols. of SO_2 introduced into the chambers thus amounts to

$$79+\frac{79}{21}x+x=79+\frac{100}{21}x.$$

x was stated to form 5 per cent. $=\frac{1}{20}$ of this volume.

We have thus the equation

$$x=\tfrac{1}{20}\left(79+\frac{79}{21}x\right)=\frac{79}{20}+\frac{5}{21}x.$$

From this follows

$$x-\frac{5}{21}x \text{ or } \frac{16}{21}x=\frac{79}{20},$$

$$x=\frac{79\times 21}{20\times 16}=5{\cdot}18 \text{ vols.};$$

that is, besides the theoretical quantities of gas mentioned above, another 5·18 vols. of oxygen, along with the corresponding $5 \cdot 18 \times \frac{79}{21} = 19 \cdot 50$ vols. of nitrogen, are necessary. The gaseous mixture formed in the sulphur-burner accordingly ought to contain upon each

$$\begin{array}{rll} 14 & \text{vols. of} & SO_2, \\ 7 + 5 \cdot 18 = 12 \cdot 18 & \quad ,, & O, \text{ and} \\ 79 + 19 \cdot 50 = 98 \cdot 50 & \quad ,, & N. \\ \hline 124 \cdot 68 & \text{vols.} & \end{array}$$

From this the following composition for 1 litre of this gaseous mixture is computed :—

$$\begin{array}{lll} 0 \cdot 1123 & \text{litre} & SO_2 \\ 0 \cdot 0977 & \quad ,, & O \\ 0 \cdot 7900 & \quad ,, & N \\ \hline 1 \cdot 0000 & \quad ,, & \end{array}$$

According to the densities of the single gases mentioned above, 1 litre of this mixture at 0° C. and 760 millims. mercurial pressure must weigh

$$0 \cdot 1123 \times 2 \cdot 8731 + 0 \cdot 0977 \times 1 \cdot 4298 + 0 \cdot 7900 \times 1 \cdot 2562 = 1 \cdot 4547 \text{ grm.}$$

Now gases, on their temperature being raised, the pressure remaining the same, for each 1° C. expand by $\frac{1}{273}$ of the volume occupied at 0°. 1 litre of 0° C. thus at t° C. (the pressure remaining unchanged) furnishes

$$1 + \frac{t}{273} = \frac{273 + t}{273} \text{ litre.}$$

If we assume the temperature of the gaseous mixture in the pipe leading from the burners = 100° C., which no doubt is below the truth, there would be formed

$$\frac{273 + 100}{273} = 1 \cdot 3663 \text{ litre}$$

from each litre at 0° C. and equal pressure; and these, of course, would equally weigh 1·4547 gram at a pressure of 760 millims.

1 litre of the gaseous mixture at 100° C. and 760 millims. pressure thus weighs

$$\frac{1{\cdot}4547}{1{\cdot}3663}=1{\cdot}0647 \text{ gram.}$$

With this we shall compare the weight of air. 1 litre of atmospheric air at 0° and 760 millims. pressure weighs 1·2932, and at 20° and equal pressure furnishes

$$\frac{273+20}{273}=1{\cdot}0733 \text{ litre};$$

it therefore weighs $\frac{1{\cdot}2932}{1{\cdot}0733}=1{\cdot}2049$ gram.

Thus atmospheric air at 20° is much heavier than the gaseous mixture in the sulphur-burner. Even at an extraordinarily high atmospheric temperature, such as 35°, the weight of the latter still exceeds a good deal that of the gas; for, as $\frac{273+35}{273}=1{\cdot}1282$, 1 litre air at 35° and 760 millims. is

$$\frac{1{\cdot}2932}{1{\cdot}1282}=1{\cdot}1463 \text{ gram.}$$

The aqueous vapour always present in the air was not required to be taken into account, since by its expansion in the heat of the burner it can only increase the difference between the weight of the gas and that of the air.

Owing to the fact that the gaseous mixture in the vertical pipe of the sulphur-burner is lighter than air, it must issue out of the top of the pipe into the chamber with a speed corresponding to the excess pressure of the atmosphere acting upon it from below. It must therefore by itself exercise a pressure upon the gas in the lead chamber. Its speed or the draught increases with the height of the vertical pipe; and the latter therefore ought to enter into the chamber-side as high up as possible. By thus securing more than sufficient drawing-power the supply of air is secured in any case; and its excess can always be moderated by narrowing the area of the inlets.

A second cause of draught is the formation of sulphuric acid itself, as the space occupied by the consumed gas cannot remain empty, and must at once be filled again. The condensation of the gas to sulphuric acid thus acts as an aspirator.

A third cause of draught is the vertical pipe taking the gas away from the last lead chamber, or the chimney with which it is connected. As the gas in these contains all the nitrogen introduced into the chambers with only 5 per cent. of oxygen, as it is saturated with aqueous vapour, and as it is usually warmer and never can be colder than the atmospheric air, it must necessarily be lighter than the latter: this is evident without any calculation.

If the nitrogen-acids are not recovered by a special process, to be explained later on, the gas certainly contains a little of those acids and of sulphurous acid, by which their specific gravity is somewhat increased. We shall, however, see that that influence is very slight, and does not materially interfere with the causes producing a decrease of the specific gravity.

The draught produced by all the above-mentioned causes regulates the quantity of air which can enter the apparatus by openings of a certain size. We have already seen that we must not introduce the exact quantity of air required for transforming the burnt sulphur into SO_3, but a certain excess, which we have calculated $=5{\cdot}18$ vols. of oxygen upon each 14 vols. of SO_2. With this, for each 14 vols. of SO_2,

$$\begin{array}{rrl} 14+7+5{\cdot}18=21+ & 5{\cdot}18=26{\cdot}18 & \text{vols. oxygen,} \\ \text{and } 79+19{\cdot}50= & 98{\cdot}50 & \text{,, nitrogen,} \\ \hline \text{together} & 124{\cdot}68 & \text{,, atmospheric air,} \end{array}$$

must be introduced into the chambers. From this it follows that for each vol. SO_2 $\frac{124{\cdot}68}{14}=8{\cdot}906$ vols. of air are required. Now 1 litre of SO_2 at 0° and 760 millims. pressure weighs 2·8731 grams, and SO_2 consists of equal parts by weight of sulphur and oxygen. Accordingly 1 litre of SO_2 at 0° and 760 milllims. contains

$$\frac{2{\cdot}8731}{2}=1{\cdot}43655 \text{ gram sulphur,}$$
$$\text{and } 1{\cdot}43655 \text{ ,, oxygen.}$$

Thus for each 1·43655 gram of sulphur burnt 8·906 litres air at 0° and 760 millims. are required. Since

$$1{\cdot}43655 : 1000 :: 8{\cdot}906 : x,$$

each 1000 grams or 1 kilogram sulphur requires $\frac{8906}{1\cdot43655}=6199$ litres air at 0° and 760 millims. pressure to be introduced into the sulphur-burner, weighing $6199\times1\cdot2932=8017$ grams or 8·017 kilograms.

For calculating the volume of air at different temperatures and pressures we must introduce the well-known formula: viz., for a temperature t° C. and a barometrical height b (in millimetres) the volume V (at 0° and 760 millims.) becomes

$$\frac{(273+t)\mathrm{V}\times760}{273\times b}.$$

For instance, at 20° and 760 millims. the calculation shows 6653 litres.

All the above calculations refer to dry air; but as the atmosphere is never free from moisture, we must take this into account. If a gas is saturated at the pressure b with aqueous vapour, its own tension is diminished by that of the vapour, and becomes $b-e$, if e be the tension of the vapour alone; so that the mixture now has the same tension as the gas previously had by itself. Thus from the volume $\frac{(273+t)\mathrm{V}\times760}{273\times b}$ the new volume V′ for gas saturated with moisture calculates as $\mathrm{V}'=\frac{(273+t)\mathrm{V}\times760}{273(b-e)}$.

The volume V′ of the 6199 litres of dry air at 0° and 760 millims., on being saturated with moisture and the temperature raised to 20° C. (at which aqueous vapour has a tension of 17·391 millims. of mercury), calculates for 760 millims. pressure as

$$\frac{(273+20)\times6199\times760}{273(760-17\cdot391)}=\frac{293\times6199\times760}{273\times742\cdot609}=6809 \text{ litres.}$$

The above calculations have thus shown that each kilogram of pure sulphur burnt for producing sulphuric acid requires a supply of

6199 litres dry air at 0° C. and 760 millims. pressure,
of 6199 + 454 = 6653 „ „ 20° „ „ „
„ 6653 + 156 = 6809 „ air saturated with moisture at 20° C. and 760 millims. pressure.

The last increase of 156 litres is only fully realized in the exceptional case of air completely saturated with moisture. As this increase is only 2·34 per cent. of the volume of the necessary dry air, whilst, according to the calculation on p. 235, about 24·68 per cent. of the theoretical quantity of air (that is, more than ten times as much) is introduced in excess, the changes in the moisture of the air and the differences of volume resulting therefrom are of no practical consequence. We shall therefore not enter into a calculation of the differences caused by the real percentage of moisture in the air.

Of course the volume of air necessary for a certain consumption of sulphur is also dependent upon the elevation of the site above the level of the sea, which regulates the mean barometrical pressure. Thus at Munich a quantity of air occupies a space larger by 5·5 per cent. than the same quantity at Marseilles.

It is easy to introduce the minimum of air required for proper work. But this is not all; an excess of air is just as hurtful as a deficiency, although not to the same extent. Air in excess cools the gas, and thus may sometimes interfere with the process; it fills a portion of the chamber-space and renders it inoperative; it dilutes the gas and weakens the energy of the chemical action. The regulation of the supply of air must therefore be accurate, and must be adapted to the frequent variations in the state of the atmosphere. This must be done by great attention in enlarging or diminishing the openings serving for introducing the air and for taking away the gas. By either means the supply of air can be diminished; but it is not indifferent which of them is selected. By the latter the draught acting upon the contents of the chambers at the end of the apparatus, by the former the pressure upon the contents of the chambers at the beginning of the apparatus is lessened. In the latter way the pressure inside the chambers is increased; in the former way it is diminished. Accordingly, if the chimney-draught is too much cut off, the gas issues forcibly from any openings in the chambers &c., whilst the air may enter properly by the holes in the front of the sulphur-burners. If, however, these latter are stopped up too far, the chambers suck in air in any places not completely closed against the atmosphere.

The draught can also be increased in two different ways, viz. by enlarging the opening in the exit-tube, or by increasing the inlet-holes in the door of the burner. Then the chambers, if the exit-tube is not sufficiently closed, suck in air; if, on the other hand, the inlet-openings are too wide, gas is forced out from any leaks in the chambers by the excess pressure. This is especially noticed when the doors are opened for charging. Both can be avoided by arranging a certain proportion between the inlet and the outlet openings. Usually (according to Schwarzenberg) the area of the latter is two thirds of that of the former. For the changes of draught made necessary by the variations in the state of the atmosphere no certain rules can be given; observation and practice must come into play here. In well-arranged works, however, this is not left to chance, but the supply of air is checked by regularly estimating the oxygen in the escaping gas, as we shall see later on.

2. *Composition of the Burner-gas, Draught, and Quantity of Air necessary in burning Pyrites.*

The same considerations as influence the draught in sulphur-burners are also valid in burning pyrites. But the proportion of air required is very much altered. We shall calculate this for pure iron bisulphide. This body consists of

1 at. iron	$Fe = 56$	$= 46{\cdot}66$	per cent.
2 „ sulphur ...	$S_2 = 64$	$= 53{\cdot}33$	„
	$FeS_2 = 120$		

Although on burning dense pyrites sometimes the iron is not all oxidized up to Fe_2O_3, and a little magnetic oxide, Fe_3O_4, is formed, we must suppose the complete conversion of iron into Fe_2O_3 as the normal state to be aimed at for complete utilization of the sulphur. Consequently 2 mols. or 240 pts. of FeS_2 require 3 atoms $= 48$ pts. O for oxidizing the iron, and another 8 atoms $= 128$ pts. O for burning the S into SO_2. Altogether 11 atoms $= 156$ pts. oxygen are necessary for burning, and another 4 atoms of oxygen $= 64$ pts. for changing the formed 4 mols. $= 256$ pts. of SO_2 into SO_3. From this we calculate:—

1. That for each thousand parts of FeS_2,

200 pts. oxygen are required for oxidizing the iron,
$533\frac{1}{3}$ „ „ „ forming SO_2,
$266\frac{2}{3}$ „ „ „ oxidizing this to SO_3,
1000 „ in all; and,

2. That for each 100 pts. of sulphur employed as FeS_2,

375 pts. oxygen must be supplied for oxidizing the Fe,
1000 „ „ „ forming SO_2,
500 „ „ „ oxidizing this to SO_3.

Since 1 litre of air at 0° and 760 millims. pressure weighs 1·4298 gram, at this temperature and pressure

375	grs.	O give	262·3	lit., mixed	in the air	with	986·7	lit. N,
1000	„	„	699·4	„	„	„	2631·1	„
500	„	„	349·7	„	„	„	1315·5	„
1875	„	„	1311·4	„	„	„	4933·3	

Accordingly, theoretically, for each kilogram of sulphur consumed as FeS_2 $1311{\cdot}4+4933{\cdot}3=6244{\cdot}7$ litres air at 0° and 760 millims. pressure must be supplied.

Now here also an excess of oxygen must be used, even larger than in the case of brimstone, which Schwarzenberg states to amount to 6·4 per cent. by volume in the gas leaving the chambers. If we call the unknown volume of oxygen in excess to be introduced for each kilogram of S employed as FeS_2, x litre, the volume of nitrogen accompanying it is $\frac{79}{21}x$ litre. Both together and the 4933·3 litre N introduced along with the O requisite for combustion and formation of SO_3 form the gaseous mixture escaping at the end, the volume of which is therefore

$$4933{\cdot}3+x+\frac{79}{21}x=4933{\cdot}3+\frac{100}{21}x.$$

As x is $\frac{6{\cdot}4}{100}$ of this volume, we have

$$x=\frac{6{\cdot}4}{100}\left(4933{\cdot}3+\frac{100}{21}x\right),$$

$$x=454{\cdot}1.$$

Accordingly for each kilogram of S burnt as FeS_2, apart from the theoretical 6244·7 lit. air, another 454·1 lit. oxygen along with $\frac{454{\cdot}1\times 79}{21}=1708{\cdot}4$ nitrogen—that is, 2162·5 lit. air—altogether 8407·2 lit. air at 0° and 760 millims. pressure have to be introduced.

Now we have found that each kilogram of free sulphur (brimstone) requires 6199 litres air at 0° and 760 millims.; consequently a certain quantity of sulphur, burnt as FeS_2, requires

$$\frac{8407 \cdot 2}{6199} = 1 \cdot 356 \text{ times}$$

as much air as if burnt in the free state.

This is not quite the proportion of the gas *as it enters the chambers*. For on burning FeS_2 a portion of the oxygen remains behind with the iron, whilst on burning brimstone the whole quantity of air gets into the chambers, and at equal temperature and pressure retains its volume, since oxygen on combining with S to SO_2 does not change its volume.

The 8407·2 litres air entering the burner for each kilogram of sulphur burnt as FeS_2, furnished the following quantities of gas, calculated for 0° and 760 millims.:—

699·4 lit. SO_2 generated from the same volume of O,
349·7 „ O required for transforming SO_2 into SO_3,
454·1 „ O as excess,
4933·3 „ N accompanying the theoretically necessary oxygen,
1708·4 „ N „ „ excess of oxygen,

8144·9 lit. containing 699·4 lit. SO_2,
803·8 „ O,
6641·7 „ N.

Consequently 100 volumes of the normal gaseous mixture on entering the chamber ought to consist of

8·59 vol. SO_2,
9·87 „ O,
81·54 „ N.

In many factories the sulphurous acid is much below 8·59 per cent., sometimes not above 6 per cent. of the volume of the gas. In that case so much less acid is made in the same chamber-space, unless the formation of sulphuric acid is increased by a larger consumption of nitre.

1 litre of the above gas at 0° and 760 millims. weighs

$$0 \cdot 0859 \times 2 \cdot 8731 + 0 \cdot 0987 \times 1 \cdot 4298 + 0 \cdot 8154 \times 1 \cdot 2562 = 1 \cdot 4122 \text{ grm.},$$

whilst the 1 litre of the gas resulting from the combustion of brimstone, according to our former calculation, weighs 1·4547. The former being, under equal conditions, lighter than the latter, consequently gives stronger draught.

For a certain quantity of sulphur, burnt as FeS_2, $\frac{8144·9}{6199}$ times $=1·314$ times as much gas must enter the chambers as if the sulphur were burnt in the free state. This figure will permit a comparison of the results of the two processes.

The preceding calculations, taken from Schwarzenberg's treatise, must be supplemented by some remarks. All practical men agree with him that a certain excess of oxygen is required, over and above the theoretical quantity, in order to promote and hasten the regeneration of nitric oxide to nitrous acid, &c. Bode ('Beiträge,' p. 15) assumes as a minimum 6 per cent. of free oxygen in the exit-gas of the chambers, and mentions that at 8 per cent. free oxygen his yield had been just as good, his consumption of nitre even a shade better than at 6 per cent. According to Hasenclever (Hofmann's Report, i. p. 370), in 1866, before Schwarzenberg, Gerstenhöfer had already calculated the theoretically best composition of burner-gas, but had only communicated it privately to several factories. His figures, which do not materially differ from Schwarzenberg's are:—for brimstone,

10·65 per cent. by volume of SO_2,
10·35 „ „ „ O,
79·00 „ „ „ N;

for burning pyrites,

8·80 per cent. by volume of SO_2,
9·60 „ „ „ O,
81·60 „ „ „ N.

Scheurer-Kestner also assumes that the percentage of oxygen in the exit-gas = 6 per cent. He has, however, proved that the oxygen in the *burner*-gas is considerably less than according to the above calculation, probably owing to the formation of SO_3 (see below).

The above is certainly controverted by some. Vogt contends (Dingl. Journ. ccx. p. 105) that there ought to be only 3 or 4, never above 5 per cent. oxygen in the escaping chamber-gas; beyond 5 per cent. he calls "very bad work." This opinion is not shared by other practical men. The other extreme is found at Tennant's works, where it is believed that the best yield of sulphuric acid is obtained with 10 per cent. of oxygen in the exit-gas, certainly with a somewhat larger consumption of nitre than when 5 or 6 per cent. of oxygen is adhered to (4 per cent. of $NaNO_3$ upon the charge of sulphur, instead of 3 per cent.). The neighbouring works, burning the same pyrites under identical conditions, only allow 5 to 6 per cent. oxygen.

But if it is established that a certain excess of oxygen, although its presence increases the volume of gas, yet also increases the energy of the action in the chambers, it is, on the other hand, at least as well established that too great an excess of air greatly diminishes the yield and seriously increases the consumption of nitre. We here refer to the account of Olivier and Perret's first trials with pyrites (p. 83).

The upper limit of the excess of air has not yet been accurately defined; but 6·4 per cent. oxygen in the exit-gas, taken by Schwarzenberg as the basis of his calculations, must at any rate be considered very suitable for practical work. Accordingly a percentage of 8·59 SO_2 by volume in the burner-gas might be considered normal (Bode with 6 per cent. oxygen in the exit-gas arrives at 8·93 SO_2 in the burner-gas as a maximum), if the following considerations did not somewhat modify this result.

In the pyrites-burner, besides sulphurous acid, there is always *sulphuric anhydride* formed during the burning. This fact has long been known, and was explained in 1852 by Woehler and Mahla, and again in 1856 by Plattner ('Die metallurgischen Röstprocesse') after many experiments, in this way—that many substances, one of which (ferric oxide) is present in large quantity in the pyrites-burner, dispose sulphurous acid to combine with the oxygen of the air to form sulphuric anhydride. We have already seen, and shall in the 17th Chapter see it in detail, that this reaction, which is most strongly exerted by finely divided platinum, can be used for the production of sulphuric anhydride itself. Another plausible explanation is, that in the cooler parts of the pyrites-burners sulphates of iron are formed, which at the hotter parts again split up into Fe_2O_3 and SO_3. This explanation, however, is not sufficient for Fortmann's experiments (Dingl. Journ. clxxxvii. p. 155), according to which the whole of the fumes of anhydride appear the moment the pyrites take fire. Lastly

Scheurer-Kestner (Bull. Soc. Chim. 1875, xxiii. p. 437) explains the matter from the well-known fact that ferric oxide can act as an oxidizing agent by successively giving up and absorbing oxygen. None of these explanations fits exactly, especially because it is established that even on burning pure sulphur a little anhydride is formed (Fortmann, *loc. cit.*).

In Fortmann's experiments, made on a small scale, on burning pyrites far more SO_3 than SO_2 was formed, viz. in one experiment 4 times as much, in another as 5 : 3. Bode doubts whether Fortmann's results would hold good on the large scale, where the conditions are different and where the formation of such an enormous quantity of sulphuric anhydride would have been detected before. Scheurer-Kestner (*loc. cit.*) only found 2 or 3 per cent. of all the SO_2 converted into SO_3, but a larger deficiency of oxygen in the gas than corresponds to this amount; and the later discussion between Bode (Dingl. Journ. ccxviii. p. 325) and Scheurer-Kestner (ib. ccxix. p. 512) has not cleared up the matter. In the last place, Scheurer-Kestner indirectly calculates from the oxygen that the sulphur of the pyrites is thus disposed of—

As SO_2 in the burner-gas	65·5
„ SO_3 „ „	32·5
„ $Fe_2(SO_4)_3$ in the burnt ore	2·0
	100·0;

but he does not explain why, of the quantity of SO_3 calculated from the deficiency of oxygen, less than one tenth is actually found in the gas; and it thus seems to be established that this indirect calculation of the SO_3 from the oxygen contained in the burner-gas is inadmissible. Bode found afterwards (Dingl. Journ. ccxxv. p. 280) in three samples of gas from a shelf-burner:—

	a.	*b.*	*c.*	
Oxygen	11·80	10·65	11·94	p. c. by vol.
SO_2	6·20	6·35	6·55	„
N	82·00	83·00	81·55	„

To the N corresponds atmospheric oxygen

21·73	22·00	21·60

Oxygen actually used for burning (if all Fe is burnt into Fe_2O_3):—

	a.	b.	c.	
For SO_2	6·20	6·35	6·55	p. c. by vol.
„ Fe_2O_3	2·32	2·38	2·46	„
Directly found as O	11·80	10·65	11·94	„
Total	20·32	19·38	20·95	„
Calculated	21·73	22·00	21·60	„
Therefore deficiency of oxygen	1·41	2·62	0·65	p. c. by vol.

This latter quantity may have been used for forming SO_3.

In order to decide the question of the formation of SO_3 on burning pyrites by more exact methods than those hitherto used, especially by Fortmann, the author, together with Salathe, made a series of experiments (Deutch. chem. Ges. Ber. x. p. 1824). It was found that SO_3 cannot, as Scheurer-Kestner had supposed, be absorbed and estimated by barium chloride, because even chemically pure SO_2 with $BaCl_2$ in the presence of O or atmospheric air at once gives a precipitate of $BaSO_4$. Check tests proved that exact results were obtained by conducting the gas through an excess of standard iodine solution, retitrating the latter by sodium arsenite, and estimating the total sulphuric acid formed in another portion of the liquid by precipitation with $BaCl_2$. By the retitration the quantity of SO_2 absorbed, by subtracting this from the total sulphuric acid that of the SO_3 was found. Two experiments with burning Spanish cupreous pyrites, containing 48·62 per cent. of sulphur, in a glass tube in a current of air gave

	I.	II.	
Sulphur obtained as SO_2	88·02	88·78	p. c.
„ „ SO_3	5·80	6·05	„
„ in the residue	3·43	5·17	„
„ lost	2·75		

Of the sulphur of the burner-gas itself there were present

	I.	II.	
As SO_2	93·83	93·63	p. c.
„ SO_3	6·17	6·37	„

Two other experiments were made in this way:—In the glass tube 50 grams of cinders from the same pyrites, in pieces of the size of a pea, were completely freed from sulphur by ignition, and fresh pyrites burnt as before, the gas passing through the cinders. Found:—

	III.	IV.
Sulphur as SO_2	79·25	76·90
„ SO_3	16·02	16·84
Residue and loss	4·73	6·26

Of the sulphur of the burner-gas itself there were present:—

	III.	IV.
As SO_2..........................	83·18	82·00 p. c.
„ SO_3..........................	16·82	18·00 „

On the large scale the formation of SO_3 will hardly be as much as in the last two experiments, because in the burners the gas passes through much less ignited ferric oxide than in our experiments.

The fact of the formation of anhydride is undisputed, although as to its quantity opinions still differ. This must also influence the percentage of SO_2 in the burners, making it appear less, inasmuch as, first, the SO_2 already transformed into SO_3 is not shown by analysis, and, secondly, because the excess of oxygen necessary for its formation, along with its nitrogen, dilute the gas. Quantitatively, this cannot yet be taken into account, because no accurate data exist. But the deviations in the quantity of oxygen from the quantity calculated are very considerable, as Scheurer-Kestner has found from his own and Büchner's analyses (Deutsch. chem. Ges. Ber. vii. p. 1665); Bode also has proved this (*loc. cit.*).

Another source of dilution of the burner-gas, likewise not traceable quantitatively, is this—that the burnt ore does not contain pure Fe_2O_3, but sulphates of iron. Whether these are ferrous or ferric sulphate, they will always retain more oxygen than Fe_2O_3, and the nitrogen corresponding to this excess of oxygen must be found in the burner-gas. On the other hand, a little nitrogen will have to be deducted if in the burnt ore FeS is present; but this amounts to very little indeed.

Lastly, in the factories working with nitre mixtures immediately behind the burners, the dilution of gas caused thereby must be accounted for. The calculated density of NO_3H is 2·17823; we need only take this into account, as the NO_3H forms the largest portion of the gas given off by the nitre mixture. It differs so little from that of SO_2 (viz. 2·21126), that, looking at the small quantities in question, we can take the two as equal without any sensible error. Now in normal working order, and using a Gay-Lussac tower, certainly not above 5 per cent. of nitre on the burnt sulphur is consumed (corresponding to 3·7 per cent. of NO_3H), or 1·85 upon the SO_2. Thus a gaseous mixture which, without the nitric acid, contains 8·59 per cent. of SO_2, contains besides $\frac{1·85 \times 8·59}{100}$ nitric acid vapour, which increases its volume to 100·1589, and diminishes the percentage of SO_2 in the total volume to 8·576—a diminution too slight to be traceable by analysis. Even if the nitric acid does not occur as such, but as NO_2 or N_2O_3, it has no sensible influence upon the analyses, even if the sample of gas is taken in a place where the "nitrous acid" coming from the Gay-Lussac tower has already entered into the process.

Still all the above-mentioned causes concur in somewhat diminishing the percentage of SO_2 in the burner-gas; so that the figures stated by Schwarzenberg, viz.

11·23 per cent. by volume in burning sulphur,
8·59 „ „ „ pyrites,

must be looked at as *maximum* figures, which in practice can only be approached, but hardly ever reached, and which never ought to be exceeded.

If the sulphurous acid in the burner-gas be estimated, this will sufficiently test the style of burning, since the oxygen of the gas must necessarily be in inverse proportion to its sulphurous acid—although not exactly, as the sulphuric anhydride comes into play. In practice, usually from 11 to 13 per cent. of oxygen is found in good burner-gas.

The innumerable observations made upon the percentage of burner-gas in chemical works during recent years have proved that with very good pyrites the above maximum figures can be very nearly approached, whilst with other ores, badly burning or containing unfavourable metallic sulphides, only 7 to 7½ per cent. SO_2 in the burner-gas is attained (*e.g.* Büchner, Dingl. Journ. ccxv. p. 557). Of course, looking at the difficulty of keeping the evolution of gas exactly equal, the different observations made in the course of a day will frequently yield less than the above figures (*e.g.* Scheurer-Kestner, in Dingl. Journ. ccxix. p. 117, in one day found 6·5, 6·5, 6·0, 8·0, 9·0, 8·7); and they only signify the *average* percentage of the burner-gas. As a *minimum*, below which the gas of real pyrites ought never to fall, 6—as ordinary average, 7 to 8 per cent. SO_2 by volume can be assumed. If less is found, the draught should be cut off; if more, more air should be admitted.

All the above calculations only refer to pyrites proper—that is, containing only a few per cent. of other metallic sulphides. If the latter have to be roasted by themselves (for instance, preparatory to their metallurgical utilization), only poor gas can be obtained, partly because more sulphates remain in the residue, for which the corresponding nitrogen is found in the gas, partly because they must be roasted altogether with a larger excess of air.

According to Bode ('Gloverthurm,' p. 88), at Oker, poor ores with 27 per cent. sulphur, of which only 22 per cent. was combined with iron, the remainder being present as blende and barium sulphate, yielded gas with 5·5 per cent. SO_2. Lead-matt yields gas with 5 to 5·5 per cent.; coarse copper metal (with 34 per cent. Cu, 28 per cent. Fe, and 28 per cent. S), 5·5 per cent. SO_2.

According to Wunderlich (Zeitsch. f. d. chem. Grossgew. i. p. 74), the gas at Oker contains 5 to 7 per cent. SO_2; its temperature in the case of ores rich in sulphur reaches 360°, in the case of poorer ores about 230°.

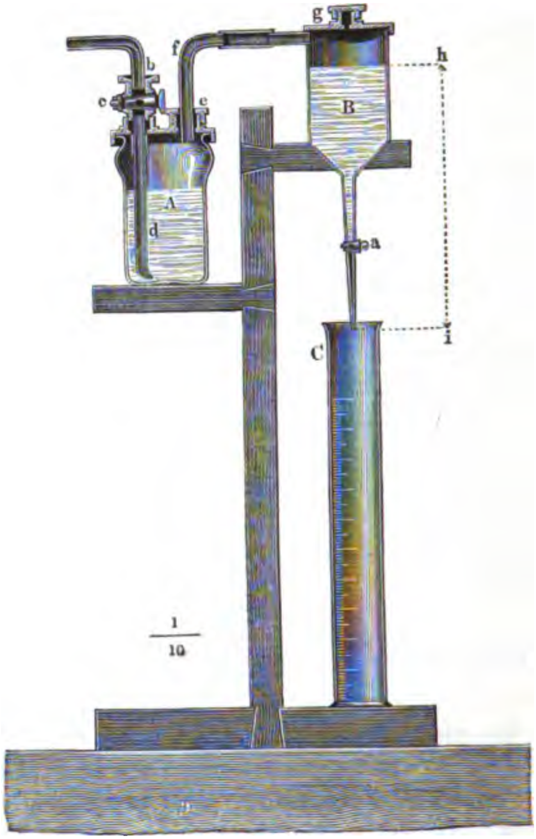
The Quantitative Estimation of Sulphurous Acid in the Burner-Gas.

This has become a very simple process, which can be carried out in a few minutes by the apparatus constructed by F. Reich in Freiberg. It has been described by its inventor, in a pamphlet published in 1858, as follows:—

The apparatus represented by fig. 99, on a scale of 1 to 10, consists of three principal parts, combined on an easily movable wooden stand. A wide-mouthed bottle, A, serves as absorbing-vessel; a cylindrical tin vessel, B, tapering below, and ending in a long, narrow tube provided with a tap, *a*, serves as aspirator; and a graduated glass cylinder, C, permits the measurement of the quantity of water run out of B.

A is closed tightly by a tin cover with two apertures. Through the first passes a brass elbow tube, *b*, provided with a cock, *c*, pierced so as to open communication between the interior of the vessel and the external air, or the other end of the tube, or to

Fig. 99.



close the interior of the vessel altogether. Into the lower part of the brass tube a glass tube, *d*, is cemented, which reaches nearly to the bottom of the vessel, but has its extremity drawn out to a fine point and bent a little. The second aperture, *e*, is provided with a cylindrical collar, and receives a cork, through which a short glass elbow tube passes. The cork must be easily taken in or out, because this has to be done at each experiment.

The tin vessel, B, has a side-tube, connected (air-tight) with the tube *f* by means of an elastic tube. In the lid there is an opening, closed by a cork, which is best tightened by a screw cap (like *e*).

When the sulphurous acid in any gaseous mixture has to be estimated, a glass tube is introduced into it, and connected with *b* by an elastic tube. The joint must be perfectly air-tight, because any fault in it cannot be discovered in the apparatus itself.

The vessel A is filled up to ⅔ or ¾ of its capacity, through *e*, with water; and B is filled almost entirely, through *g*. A small quantity of standard iodine solution is added to the water in A, along with a little starch, by which the water assumes an intensely blue colour. The cock *c* is turned so that no air can enter into A; *a* is opened, so that water runs out until the air in A and B is so far expanded that the column of water in B is supported. The water then ceases to run, provided that every thing closes air-tight; if not, the water will continue to run. When thus the apparatus has been tested, *a* is shut, and *c* turned so that *b* and *d* communicate; then *a* is opened so that the water runs out slowly, the gas to be tested entering through *d* in single bubbles, and rising through the coloured water. As soon as the SO_2 contained in it gets into the water, it converts the free iodine into iodhydric acid; and after a certain time the liquid will be decolorized, which at last happens very suddenly and can be very accurately observed. As soon as this happens, the cock *a* is closed. By this preliminary operation the whole of the inlet-tube is filled with the gas to be tested.

Now *e* is opened, and a measured volume (say, *n* cub. centims.) of standard iodine solution is put into the vessel A, by which, of course, a blue colour is again produced; *e* is closed again; *a* is cautiously opened, and water is run out till the liquid in *d*, which, on opening *e*, had risen to the level of the outer liquid, has been depressed to the point of the tube, in order to expand the gas in A up to the degree of pressure at which the following observation takes place; then *a* is quickly shut, all the water that runs out is poured away, and the empty graduated vessel C is put back into its place. Now *a* is opened, and, by the running-out of the water, gas is slowly aspirated through A, till the liquid is decolorized again, whereupon *a* is closed, and the volume of the water run out into the graduated cylinder is measured. We will call it *m* cub. centims. In this process no sulphurous acid escapes unabsorbed.

If a second testing is to be made, without any further alteration a fresh quantity of iodine solution can be put in, and the process recommenced. When this has been repeated a few times, the decolorized liquid in A, after a short time, again turns blue of itself, because then its percentage of HI has become so large that it decomposes on standing and liberates iodine. This liquid must then be poured away, and replaced by fresh water and a little starch solution.

The calculation of the result is as follows:—The n cub. centims. of iodine solution, provided it contains 12·7 grams per litre, by its decolorization shows 0·0032 gram SO_2, which, at 0° C. and a barometrical pressure of 760 millims., occupies a volume of $1{\cdot}104 \times n$ cub. centims. If the barometer shows b millims., and the thermometer t° C., and the height of the water, hi, is $=h$ millims., the exact volume of $0{\cdot}0032 \times n$ gram SO_2 is

$$1{\cdot}104 \times n \times \frac{760}{b - \frac{h}{13{\cdot}6}} \times (1 + 0{\cdot}003665 \times t) \text{ cub. centims.}$$

As the water run out, and thus also the gas aspirated through A, amounts to m cub. centims., the volume of the aspirated gaseous mixture, before the absorption of the SO_2 contained therein, must have been

$$m + 1{\cdot}104 \times n \times \frac{760}{b - \frac{h}{13{\cdot}6}} \times (1 + 0{\cdot}003665 \times t) \text{ cub. centims.,}$$

and the percentage of SO_2 in volumes of the gaseous mixture

$$\frac{100 \times 1{\cdot}104 \times n \times \frac{760}{b - \frac{h}{13{\cdot}6}} \times (1 + 0{\cdot}003665 \times t)}{m + 1{\cdot}104 \times n \times \frac{760}{b - \frac{h}{13{\cdot}6}} \times (1 + 0{\cdot}003665 \times t)}.$$

In most cases a correction for the barometrical and thermometrical changes will not be required; and the formula is then simply

$$\frac{110{\cdot}4 \times n}{m + 1{\cdot}104 \times n} \text{ per cent. } SO_2.$$

If the percentage of SO_2 in the gas is very small, and thus m very large in proportion to n, the formula may be simplified into

$$\frac{110 \cdot 4 \times n}{m}.$$

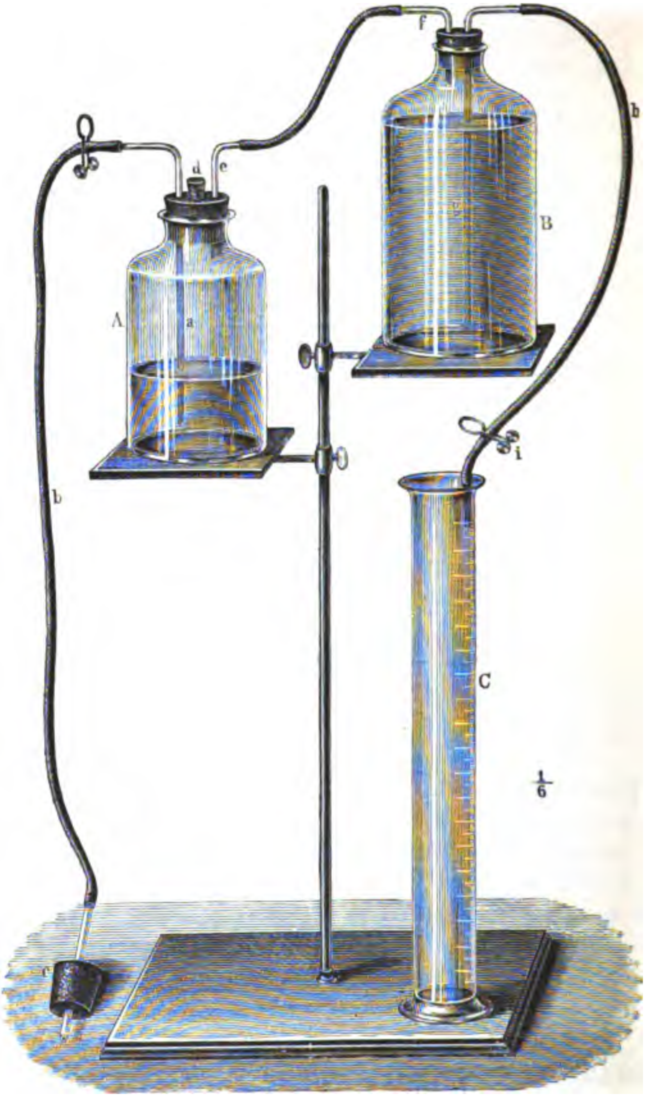
Instead of Reich's apparatus, with its tin and brass parts, the following apparatus, made of glass bottles, glass tubes, and india-rubber corks, can be employed, which is both cheaper and more durable:—

A (fig. 100) is a wide-mouthed bottle of about 1 litre capacity, provided with a three-times perforated india-rubber cork. Through one perforation passes the glass tube *a*, which, by means of the elastic tube *b*, serves for introducing the gas; for this purpose a hole is drilled into some convenient part of the burner-pipe, and the india-rubber cork *c* exactly fitted into it. The second, somewhat wider perforation is closed by the small plug *d*; through the third the elbow tube *e* passes, which is connected with the corresponding tube *f* of the bottle B, holding 2 or 3 litres. The latter serves as an aspirator—the glass tube *g*, reaching to its bottom, being continued into an elastic tube *h*, closed by the pinchcock *i*, the whole when once filled serving as a siphon. The graduated cylinder, C, holds 250 cub. centims.

The operation is exactly the same as with Reich's own apparatus, but with the advantage that after opening the plug *d* a certain quantity of iodine solution can be easily run in, and the opening can at once be closed, a little water and starch solution having been previously added. When the cork *c* has been inserted in the gas-pipe, the pinchcock *i* is opened with the right hand, and at the same time the bottle A is shaken up during the passage of the gas-bubbles. The moment the blue colour of the iodized starch has gone, the pinchcock is closed, so that no more bubbles of gas can pass through. The bottle A need not be emptied, so long as it has not become too full; but a new analysis can be made at once, after a fresh quantity of iodine solution has been added.

If 10 cub. centims. of a decinormal iodine solution (=12·7 grams in 1000 cub. centims.) have been put into A, this quantity, according to the above-given formula, will correspond to 0·032 gram, or 11·14 cub. centims. SO_2, at 0° C. and 760 millims.; and this number

Fig. 100.



need only be multiplied by 100, and divided by the number of cub. centims. of water collected in C, *plus* 11, in order to find the percentage of SO_2 in the gas. The barometrical and thermometrical corrections are in this case, of course, neglected. The following Table will save this calculation. On employing 10 cub. centims. of decinormal iodine solution, the following number of cub. centims. collected in the graduated cylinder, C, show :—

cub. centims.	Volume percentage of SO_2.
82	12·0
86	11·5
90	11·0
95	10·5
100	10·0
106	9·5
113	9·0
120	8·5
128	8·0
138	7·5
148	7·0
160	6·5
175	6·0
192	5·5
212	5·0

Even if the gas to be examined is taken at a point where it is already mixed with nitre-gas, this will not exercise any practically important influence upon the result. We have already seen that, in ordinary work, for each 100 parts of SO_2 only 1·85 NHO_3, or its equivalent as N_2O_3 or NO_2, exists in the gas. In such dilute aqueous solutions as come into question here nitric acid hardly at all oxidizes sulphurous acid; this, however, is done by nitrous and hyponitric acids. Even if we assume that only NO_2 is formed (which is going much too far), this could at most oxidize its equivalent in SO_2, according to the formula

$$NO_2 + H_2O + SO_2 = SO_4H_2 + NO.$$

46 NO_2 thus oxidizes 64 SO_2, or 1·35 NO_2 (the equivalent of 1·85 NO_3H) only 1·88 SO_2; in other words, in the worst case, never happening in practical work, of 100 parts SO_2 1·88 part would be oxidized by nitrogen acids instead of iodine. Even this maximum error would, say, at 10 per cent., only amount to a deficiency of 0·188 per cent.; but this is certainly reckoning it much too high.

With nitrous acid the error would only amount to one half of the above. It will become a little larger if the sample of gas be not, as is preferable, taken before entering the Glover tower, but afterwards, where the nitrous gas from the nitrous vitriol is already mixed with it. But if a gas has to be examined which contains very little sulphurous acid, and nitrogen-acids besides, such as the gas escaping from the chambers into the chimney, Reich's test is not applicable, because blue iodized starch is constantly reformed.

Estimation of Oxygen in Burner-Gas and Chamber-Gas.

This estimation is only made exceptionally on burner-gas (latterly more often than formerly), but all the more frequently on the gas leaving the chambers; and, for the sake of connexion, it will be described here at once. Of course, an analytical process to be employed in factories must be carried out quickly, and with little apparatus; and for this reason Bunsen's eudiometrical method is hardly applicable in this case. It is, moreover, not called for, as we know a large number of absorbents for oxygen, and at the same time we possess handy and sufficiently accurate instruments, such as Winkler's gas-burette and similar apparatus.

Among the absorbents of oxygen, one of the oldest is *phosphorus*, which, however, acts too slowly, and is consequently little employed now; P. Hart (Chem. News, xix. p. 253) gives special rules for its use. Vogt (Dingl. Journ. ccx. p. 103) employs ferrous hydrate. He collects the gas, deprived of SO_2 and nitrogen-acids by potassium bichromate and caustic potass, in a vessel of a certain size, and admits into this an acid solution of the double protosulphate of iron and ammonia, and at last ammonia. All the $Fe(OH)_2$ is thus precipitated. The absorption of oxygen is assisted by shaking; but it takes a long time and a large excess of ferrous hydrate. It is estimated either by measuring the contraction of the gas or by titrating the unoxidized ferrous oxide by permanganate.

Scheurer-Kestner's process is more convenient, but unfortunately wrong in principle (Compt. Rend. lxviii. p. 608). He makes use of Priestley's (inaccurate) observation, according to which, in a mixture containing oxygen, nitric oxide is oxidized to NO_2, which afterwards dissolves in water as equal parts of N_2O_3 and N_2O_5, or rather as the hydrates of these anhydrides. He accordingly divides the number of cub. centims absorbed by 3, in order to find the oxygen for 2 volumes NO + 1 volume O $=NO_2$. Scheurer-Kestner collects the gas in pear-shaped india-rubber vessels, provided with a cock, which are several times filled and emptied by squeezing, until the gas may be assumed to be pure. The nitric oxide is made from copper filings and nitric acid, collected over water in a graduated tube, and its volume read off. In the same trough a little of the gas to be examined is introduced into another graduated tube, read off, sufficient NO introduced from the other tube, and after a few minutes the contraction in the second tube read off. But in this no notice is taken of the long-known fact, to be dilated upon when we explain the theory of the chamber-process, that oxygen with NO not merely forms NO_2, but also N_2O_3, so that the simple proportion 1 : 3 does *not* express the proportion of absorption.

Ammoniacal cuprous chloride is employed in Orsat's apparatus, patented in 1873, which also permits the SO_2 to be estimated at the same time. To describe this apparatus would take up too much space; it is sold by all apparatus-makers. In spite of its being somewhat expensive, delicate, and not quite accurate in its results, it is certainly so very convenient for use that many works have already introduced it for the estimation of oxygen. Winkler's gas-burette is cheaper, more accurate, and more easily carried about.

The best absorbent for oxygen is an alkaline solution of *pyrogallic acid,* proposed in 1820 by Chevreul, but not until 20 years later practically introduced by Liebig. Crace Calvert (Proc. Manch. Lit. and Phil. Soc. 1863, p. 184) has objected to this reagent, that by its action on oxygen carbon monoxide is formed; but Poleck (Zeitsch. analyt. Chemie, 1869, p. 451) has shown that this only happens with pure oxygen, and never with gaseous mixtures containing not more than 20 per cent. of oxygen by volume. This process can be used with Winkler's gas-burette, or Orsat's apparatus, or with a special apparatus constructed by Max Liebig (Dingl. Journ. ccvii. p. 37), and made by Dr. Geissler in Bonn, which permits an estimation to be made in three minutes' time.

It has often been proposed to purify the gas from any sulphurous acid or nitrogen-acids (which would be equally absorbed) by the alkaline solution of pyrogallic acid, by means of potassium bichromate, or, at least, by treatment with water; but the error occasioned by the presence of these acid gases is too small to be taken into account for practical work.

The apparatus and processes for technical gas-analysis have been exhaustively treated in an excellent work by Professor Winkler ('Anleitung zur chemischen Untersuchung der Industriegase,' Freiberg, 1877), which should be consulted for particulars on this subject.

Instead of taking single samples of the escaping gas, or along with these, it is advisable to collect an average sample (say, for 24 hours) by aspirating a certain quantity (say, about 50 litres) by means of a large aspirator with the outlet-cock very slightly opened. Owing to the slowness of the aspiration, the gas standing over the water in the aspirator will be thoroughly mixed up, and by taking a sample from the aspirator the *average* percentage of oxygen can be estimated with some degree of accuracy.

Comparison of Brimstone and Pyrites as Material for Sulphuric-acid-making.

We have found above (p. 241) that the burner-gas from brimstone is richer than that from pyrites in the proportion of 1 to 1·314; that is to say, under equal conditions, the gas generated in burning pyrites occupies 1·314 times as much space as if the same quantity of sulphur had been employed as brimstone. From this it directly follows that the gas will also require as much more chamber-space; thus, for an equal production of sulphuric acid, the chambers must be about one third larger if working with pyrites than if working with brimstone. Usually it is assumed that the consumption of nitre has to be increased in a similar ratio; this, however, is not the case, as a properly constructed Gay-Lussac tower retains almost the whole of the nitre-gas, and the excess volume of air is not of great importance. Now-a-days, indeed, in well-managed works, less nitre is used with pyrites than has ever been used with brimstone. Only, as we shall see, the arsenic in the pyrites necessarily leads to a loss of nitre.

Leaving the nitre out of consideration, the advantages of using brimstone are:—a somewhat higher yield of acid (see later on); rather less cost of plant, and less trouble with the burners if any thing goes wrong; and, above all, much greater purity of the sulphuric acid, especially from iron and arsenic (though this is important only for sale acid). If brimstone could be had at the same price as the sulphur in pyrites, nobody would hesitate for a moment to employ the former; and even a moderately higher price would not deter from this; but where the pyrites-sulphur, as is the case in most industrial countries, only costs one half or even a quarter of the price of brimstone, the latter can no longer be employed, except for *pure* acid; and even this, when the difference in price is very large, can be more cheaply made from pyrites than from brimstone.

Owing to this cause, the manufacture of brimstone-acid in Europe is confined to a few small factories which make specially pure acid for bleach-works &c. In America, however, where the large demand for vitriol for the refining of petroleum has caused a large number of vitriol-works to spring up at New York, Boston, Philadelphia, and Pittsburg, the acid is almost exclusively made from Sicilian brimstone, of which, in 1876, 49,500 tons were imported into Philadelphia. It appears that the American pyrites is not very good; and if a raw material has to be brought from Europe, the question of freight must evidently decide for brimstone. Probably greater convenience and the easier kind of labour required have contributed to decide the choice in favour of brimstone.

It is frequently asserted that sulphuric-acid chambers worked with brimstone last three times as long as with pyrites. Knapp states their duration at 10 to 15 or more years. But even with pyrites the average time is from 8 to 10 years; only the first chamber wears out more quickly if the gas is not properly cooled: in most cases a Glover tower will prevent this. At Stolberg formerly, when the lead was less pure and consequently less easily attacked, the chambers, even with pyrites, lasted up to 20 years. Probably the percentage of arsenic contained in the pyrites has something to do with the duration of the chamber. So much seems clear, that chambers worked with brimstone last *somewhat* longer than if worked with pyrites.

The Draught-pipes from the Pyrites-burners leading to the Chambers

must be constructed rather differently from those employed with sulphur-burners, both on account of the flue-dust and of the higher temperature. It has been stated above that the gas escaping from the sulphur-burners has a temperature of 100° to 130° C., and that the gas-pipe must not be cooled too much. It is quite different with pyrites. Bode calculates the temperature of combustion of pyrites at 1563° C. (that is, a strong white heat). This temperature, probably, is not actually reached in the burner itself; and the gas is already cooled very much in the gas-flue above the burners; but it always remains far too hot to be taken direct to the chambers, both because this would disturb the process and because it would destroy the chambers very quickly. Scheurer-Kestner (Wurtz, Dict. de Chim. iii. p. 149) states the most suitable temperature of the gas on entering the chamber to be 60° C.; usually, however, it is rather warmer.

According to this, the gas has always to be *cooled* in some way; and many contrivances have been used for this purpose. The gas is generally conveyed in large cast-iron pipes, which are suitably shaped, as shown in fig. 101, in order that the upper half may be replaced independently of the lower one, or taken away for cleaning; the latter can also be done by means of man-holes. For a set of from 12 to 18 burners a pipe of 2 feet diameter is sufficient; but they are sometimes made upwards of 3 feet in diameter. Only rarely are they made to be lined with fire-bricks, as shown in fig. 102; the cooling in this case is very imperfect, and the cost much higher. Occasionally, in very large works, square or oblong flues of wrought or cast-iron are found. Brick flues are very unsuitable, except for perpendicular shafts or for flue-dust chambers. They are made of bricks boiled in tar, and set with tar and sand. Earthenware pipes would crack too quickly. If a Glover tower is present, the iron pipes go up to this; otherwise they are replaced by lead pipes shortly before entering into the chambers.

Fig. 101.

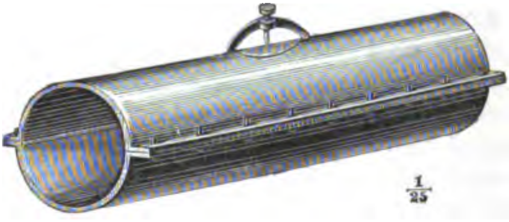
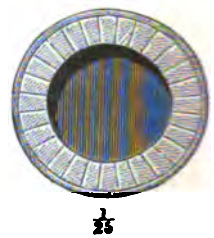


Fig. 102.



At some works the gas is simply cooled by making the draught-pipes very long, up to 300 feet: this is expensive and inconvenient. At others the pipes are led through water-tanks, or the gas passes through lead cylinders with an iron jacket and the cooling-water between them. Even more complicated contrivances for cooling have been employed; but we shall not go into them, as their special construction is of small moment, and as a Glover tower makes them unnecessary. It must be considered that the gas from pyrites-burners acts very corrosively, especially by its percentage of SO_3 or SO_4H_2, which, however, only comes into play on cooling. The more completely this is effected, the more both metals and brickwork are acted upon. A Glover tower entirely avoids this drawback, whilst cooling by acid-evaporating-pans retains it—to counteract which the pan-flues have to be made of acid-proof material.

The only rational way of cooling the gas is *to utilize the heat of the gas*; and the use made of it in most factories is *for concentrating the chamber-acid*. Formerly this was most frequently done by pans placed on the burners and gas-flues, latterly by the Glover tower, as we shall see in the following chapters.

In the gas-flues and draught-pipes *flue-dust* is always deposited, much more when smalls are burnt than with lump ore, especially in furnaces where the small ore is moved about. In such cases special dust-chambers are indispensable, as has been remarked in the description of those furnaces. Even with large lumps the flues and pipes must be cleaned out from time to time, as they would otherwise be stopped up entirely. At some factories this is done monthly, at others more rarely. If the deposit is allowed to remain too long, it hardens into a stone-like mass, which cannot be got out without stopping the process.

The composition of this deposit varies, of course, very much; and even its external aspect varies from that of a dry, light dust to that of thick, strongly acid mud. Clapham analyzed such a deposit (Richardson and Watts, Chem. Technol. i. 3, p. 73), and found:—

Sand &c.	2·333
Lead oxide	1·683
Ferric oxide	3·700
Cupric oxide	trace.
Zinc oxide	trace.
Arsenious acid	58·777
Sulphuric acid	25·266
Nitric acid	trace.
Water	8·000
	99·759

Reich ('Erdmann's Journal,' xc. p. 176) found in the Mulden Works a crystallized deposit consisting of equal molecules of arsenious acid and sulphuric acid.

In other cases the deposit is dry dust, mostly consisting of mechanically conveyed pyrites dust, better burnt than that within the burner itself (Bode, 'Beiträge,' p. 41), and nearly always containing so much arsenic that its crystals can be seen with the naked eye.

H. A. Smith ('Chemistry of Sulphuric-Acid-making') found in it 46·36 per cent. of As_2O_3, along with a large quantity of sulphur in the pasty condition—the latter, of course, formed by sublimation from pyrites.

The flue-dust is also a principal source of *thallium*, as we shall see; and when *selenium* occurs in the pyrites it is found in the flue-dust.

CHAPTER VIII.

THE LEAD CHAMBERS.

We have already seen, in our historical survey, through how many stages the construction of that apparatus has gone in which nowadays all sulphuric acid, except the Nordhausen oil of vitriol, is made, viz. the *lead chamber*. The reader already knows that sulphuric acid is formed by the oxygen of the air being transferred to sulphur dioxide through the intervention of the acids of nitrogen and with the aid of a molecule of water, thus:

$$SO_2+O+H_2O=SO_4H_2.$$

All the substances coming into question here, except the final product, are in the state of a gas or (as the water) of a vapour. The reaction takes a certain time, as the same molecule of nitrous or hyponitric acid has to be frequently reduced and reoxidized, and as the gases are only gradually mixed so intimately that they can actually enter into reaction. There must therefore be a space given in which large quantities of gas can remain for some time. According to the calculations given on pp. 231 and 238, for each kilogram of sulphur in the state of brimstone 6199, or in the state of pyrites 8145 litres of gas, reduced to 0° and 760 millims. pressure, must enter into reaction; and these figures are a good deal increased by the higher temperature, the steam, &c. In order to harbour such very large quantities of gas, very large spaces must be provided. Since the strongest acids have to be dealt with, both in the liquid and the gaseous form, most materials otherwise used in building are out of the question; and since, of those suitable, glass, earthenware, &c. are excluded by the large size of the apparatus, practically only *one* material remains which is sufficiently cheap and suitable for the purpose, viz. *lead*. The disadvantages of this metal, such as its great weight, its softness and lack of rigidity, its easy fusibility, its comparatively high price cannot outweigh the advantages which none of the base metals shares with it for our purpose, viz.:—its great chemical resistance to the acid gases and liquids; its ductility, which permits rolling it into large sheets; its extraordinary pliability and toughness, by the assistance of which it can easily be shaped in every possible way; and, lastly, even its easy fusibility, which permits the edges of two sheets to be so completely united by melting together with a strip of lead, that they form a whole for all practical purposes, so that it is possible to make vessels of indefinitely large size and any shape, provided that care be taken to support the walls of the vessel on the outside, lest they collapse by their own weight.

A special advantage of lead is this, that even after a number of years, when the chambers have become quite worn out, the greater portion of its value can be recovered by remelting the material; even the mud containing lead can be utilized.

The attempts to make sulphuric-acid chambers from other materials than lead have completely failed. To this class belongs the proposal of Leyland and Deacon (patents of September 10th and December 2nd, 1853) to make them of *hard-burnt firebricks*, slate, sandstone, basalt, &c., set with a mixture of melted sulphur and sand. *Vulcanized india-rubber* or *gutta percha* are just as useless; Krafft (Wagner's 'Jahresb.' 1859, p. 137) found that gutta percha in an acid-chamber loses six times as much weight as lead, and half as much again of its surface. It would be absolutely impossible to use it, because it softens at the temperature of the chambers, and in that state is even more easily acted upon by the gases. Simon's *zeiodelite* (Dingler's 'Journal,' clv. p. 100), a mixture of 19 sulphur with 42 pounded glass, to be employed in slabs of ½ inch thickness, has, no doubt, never been so much as tried for this purpose, no more than the *sheets of glass* proposed by Wilson and others.

We will now describe the *erection of lead chambers.*

The chambers are always placed at some elevation above the ground-level. Now-a-days, probably, chambers are nowhere found placed on the ground itself, or on such low foundations that one cannot at least walk about underneath; mostly their bottoms are much higher than this. The first object of this is to give the opportunity of ascertaining whether the chambers are tight. If their bottoms are not easily accessible, large quantities of sulphuric acid may get lost in the ground before any loss is detected. And this not merely means a loss of the acid, but still more: the foundations are corroded and undermined; and the whole structure may collapse. The expense of building the chambers on pillars &c. is not thrown away, as the whole space underneath can be used as a warehouse which in winter time has always a moderately high temperature; or it may even, if high enough, be utilized for the pyrites-kilns &c. In the latter case it should be from 17 to 20 feet high. At some works, which are pressed for space, even the sulphate-furnaces, ball-furnaces, &c. are built underneath the chambers; but the space below them in this case must be at least 30 feet high.

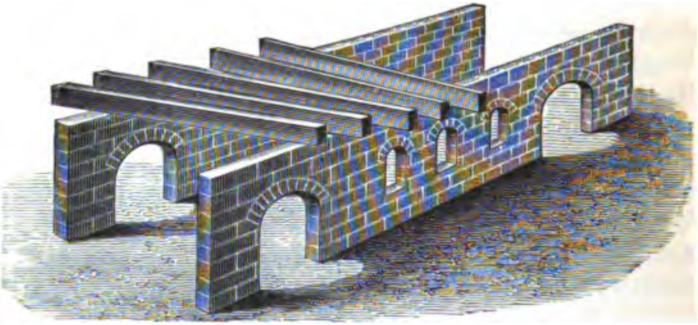
In any case the soil must first be examined to ascertain whether it affords a safe *foundation*; for if it settles more in one place than in another, the chamber gets out of plumb, and its bottom out of level, which, owing to the acid lying on the latter and on the instability of the chamber-sides, causes great inconvenience. A rocky or pebbly ground is best; next to this, sand or clay; marl or limestone are bad, because sometimes acid will run over accidentally, which acts upon it; and this may happen even with clayey soil. In such cases the whole soil underneath the chambers must be protected by a layer of asphalte.

The pillars upon which the chamber is erected must, of course, go down to the "rock," as in any ordinary higher building. If the accumulation of made ground or loose earth is so deep that it would be too costly to excavate and raise the pillars from below, piles must be driven in, according to well-known building-rules, and the pillars built upon these.

The pillars themselves can be made of brickwork, stone, cast iron, or wood. Sometimes, instead of single pillars, whole walls are found, viz. two longitudinal walls, connected by cross joists and interrupted by doors, windows, &c., as shown in the sketch, fig. 103 (p. 264). Such long walls take much material and make the room underneath the chambers dark, in spite of the windows. They are only suitable where the chambers are placed unusually high in order to build furnaces underneath. Up to a height of about 26 feet metal pillars seem preferable.

The cheapest pillars are those made of wood or bricks; very rarely they are made of stone—much more frequently of the dearer but much stronger and more durable material, cast-iron. If made of wood, round or canted balks of at least 10 inches (better 12 inches) thickness must be employed. Mostly fir or pine wood is used, especially Scotch fir; but the American pitch-pine or yellow pine, such as is used for ship-building, is preferable (on account of its much greater durability) in spite of its higher price. This applies not merely to the foundation pillars, but even more to the frame of the chamber itself. The pillars must vary in their thickness, mutual distance, and manner of being stayed, according to their height and the weight resting upon them; but for an average height of 10 to 13 feet, which will not often be exceeded with wooden pillars, they ought not to be further apart than 10 to at most 13 feet from centre to centre. In any case they are put into a stone socket projecting from the ground, lest the bottom of the pillar be damaged by any moisture or acid; the stone has at the top a hollow of ½ to 1 inch depth, into which the foot of the pillar fits exactly; at first a little tar is poured into it. Wooden pillars do not last long; they are not to be trusted very much, and are rarely found now in larger works, at any rate as principal pillars, except where wood is very cheap.

Fig. 103.



Much more frequently *brick pillars* are employed. These also are not often made above 13 feet, at most 15 feet high; they are at least 18 inches (better 2 feet) square. They are made of common bricks with a mortar very poor in lime. The mortar can be made very cheaply and of excellent quality in this manner:—A ton of alkali (tank) waste, two tons of furnace-cinders, 6 to 8 cwt. of slaked lime, and sufficient water are ground up in a pug-mill, till the mixture has become a homogeneous tough mass of the consistency of putty. This usually takes an hour. Instead of lime slaked on purpose, the lime riddlings from the bleaching-powder manufacture, which are otherwise worthless, can be used, and with equally good results. This mortar is used without any sand; it can be kept for some days, and sets very quickly and hard, much more so than ordinary mortar, and is even more resistant to acids. Thus from worthless materials, which otherwise cost some expense for their removal, a mortar of much greater value than lime mortar can be made, which, of course, can be used for any other purpose as well; its only drawback is that the joints are not white, but blackish grey, and that salts effloresce on the surface, which, however, after having been washed away a few times, do not return again. Undoubtedly the great hardness of this mortar is owing to the presence of sulphate of lime, similar to Scott's selenite mortar.

The brick pillars in many works have been replaced by cast-iron ones, because they suffer a good deal by acid running over, especially at the top, where the beams rest. Even the bricks themselves become rotten by contact with the acid, and only stand better if previously soaked in hot tar; but they take the mortar very badly after that. They can also be painted with hot tar afterwards.

On the continent, where in consequence of the colder winters and hotter summers the chambers have to be placed in a closed building, the pillars can be built in a piece with the main walls of this building; but it is even then best to keep them to themselves, as their settlement is different from that of the main walls.

Chambers 20 feet and upwards in width are sometimes built with mixed pillars—viz. brick pillars for the two long sides, and wooden pillars for the centre row.

Stone pillars are not often used for acid-chambers. Made of rough stones, they would be extremely clumsy; and hewn stone in most places is too dear. On the other hand, of course, stone pillars are very substantial, and last almost for ever, unless the stone be very soft and rotten.

In the larger works in England *cast-iron* pillars have latterly been almost exclusively employed, in spite of their higher cost. These can be made 30 or even 36 feet high; they take very little space, and are almost imperishable if painted from time to time. They can be weighted a good deal more than any other pillars, unless

Fig. 104.

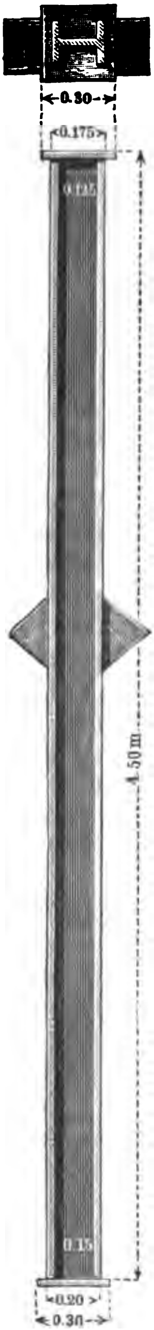
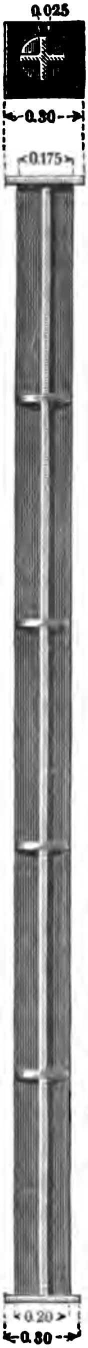


Fig. 105.



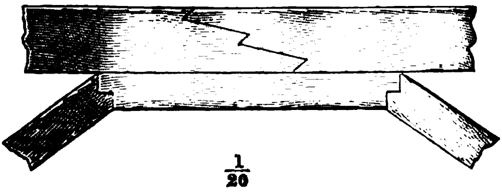
these are made very thick; and they can be used as supports for many other purposes by means of cast-on brackets or even of pieces bolted on subsequently. A brick or stone foundation must be made for them up to the level of the ground or a little higher; the top stone is made with a socket to receive the foot of the pillar, as in the case of wooden ones; or holes are drilled into the stone, corresponding to other holes in the base of the column; and the joint is made by iron cramps, fastened by pouring in melted lead, or in some other way.

The cast metal columns are now usually made of an **H**-shaped section, and a little tapering upwards. Fig. 104 will show this more distinctly, together with a bracket on each side for receiving a wooden stay for the timber above. Another, cross-shaped section is shown in fig. 105. These constructions are stronger, for an equal weight of metal, than round columns, and better adapted for brackets &c. If higher than shown in the figures (15 feet), they must be correspondingly stronger—for instance, for 20 or 24 feet height, 12 inches diameter at the base. Such columns can be placed at 20 feet distance from centre to centre, if the beams resting upon them are strong enough.

The mutual distance of the pillars across the width of the chambers is arranged in this way:—They and the beams resting upon them are just underneath the side frames of the chambers, because they support not only the sides, but also the roof of the chambers, as we shall see directly. In the case of narrow chambers this suffices; but with wider ones (say about 15 feet) a centre row of pillars must be added. On the other hand a single row of pillars, if strong enough, suffices for supporting the beams for the sides of two adjoining chambers (say the east side of one and the west side of another chamber), the distance between these usually not exceeding 5 feet. Of course this requires much stronger beams; but it effects a considerable saving in material and in space.

Above the pillars there are generally, in England, *longitudinal sleepers*. If there is a continuous wall in the place of pillars, to cover this with a 2-inch plank will be sufficient; but if there are separate pillars, the sleepers must be strong enough to support the whole structure of the chambers, both wood and lead; and their strength will then depend on the distance between the pillars. With chambers of 20 feet height, and distances between the pillars of 20 feet from centre to centre, the longitudinal sleepers ought not to be less than 12 to 14 inches high, and ought, besides, to be supported by stays, as shown in fig. 106. With the pillars at shorter distances (say 10 or 13 feet), timber of 9 by 12 inches, always on edge, suffices for the longitudinal sleepers. The joints of the beams of which they consist ought to be well connected, as shown in fig. 106, and ought to be placed between the pillars, where they are supported from below by the stays. The upper face of the sleepers must be as well levelled as possible from one end of the chambers to the other. Above these the *cross joists* are placed, running from side to side, and made long enough to carry the side frames, and to leave, moreover, a passage round the chambers. For the latter object only every third or fourth joist need project about 5 feet on each side. On the Continent the joists are usually

Fig. 106.



$\frac{1}{20}$

made square in section, in England always of planks on edge, which seems preferable, because for an equal volume of wood the support of the chamber-floor is divided over a larger area, and the erection is thus strengthened. Here also the span must be considered in fixing the strength of the wood. If chambers are much less than 20 feet wide, which rarely happens now, no centre longitudinal sleeper is needed, and the cross joists should have 9 by 3 inches section, and corresponding length. Wider chambers require a centre row of pillars and sleepers; and in this case, as such long planks are not easy to get, the joists can be made in two lengths, resting on a side and on the centre sleeper. The horizontal distance of the floor-joists is usually 12 inches from centre to centre. Some works have them 3 by 11 inches. The length of the joists is equal to the width of the chambers *plus* the chamber-frame, *plus* the width of the passage.

The joists are covered with a 1-inch floor, laid quite level in all directions. As the flooring-boards might easily warp afterwards from the heat of the chambers, this must be prevented by the well-known methods of carpentry. The edges of the boards are planed so as to form a perfectly smooth floor without any chinks.

Another system of building is more in favour on the Continent. First, from pillar to pillar strong sleepers are laid across the width of the chamber; upon this a large number of longitudinal joists are laid, and the flooring-boards on the top of these, running from one side of the chamber to the other.

Upon the whole the *frame of the chamber* is erected, which serves for supporting the lead. It consists, for each side of the chamber, of a sole tree and a crown tree, connected by uprights, and further tied by cross rails or stays. The sole- and crown-trees and uprights are either of square section (say 6 inches square for a chamber up to 20 feet high), or oblong (say 7 by 3 inches). The sole- and crown-trees lie on the flat side; and the uprights are mortised into them so that their longer side just covers the trees. In the corners the trees project over and are rabbited into each other. If no cross rails are employed, the uprights are placed 3 feet 3 inches apart from each other; if they are connected by cross rails, they can be placed 4 feet apart. The cross rails are 3 inches by 2 inches; they are only partly let into the uprights, in order not to weaken these, and are placed at vertical distances of 4 to 5 feet from each other. The chamber-lead is kept a little apart, so that the air can cool it, as otherwise it is readily corroded by the acid; even insects from the wood may penetrate it (Bode). Sometimes the cross rails are cut into particular shapes, such as those shown in figs. 107 and 108, in order to touch as little of the surface of the lead as possible. Whether cross rails are used or not, in any case there should be diagonal stays, to give more stability to the frame. It is not of much consequence how the stays are put, so long as this is done according to the well-known rules of carpentry.

Fig. 107.

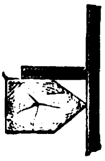
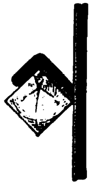


Fig. 108.



If, as is usual in England, the chambers are in the open air, one side of the frame is made about a foot higher than the other, so that the rain-water and melted snow can run off, and on the lower side a water-spout is arranged in such a way that the rain-water cannot run along the chamber-side down into the acid at the bottom.

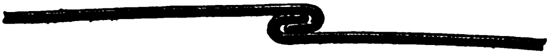
Now the *chamber* itself can be erected. For this, sheet lead as wide as the rolling-mills can supply it, and of convenient length, is used, so as to have as few seams as possible. The usual strength in England is 6 lb. to the superficial foot, sometimes 7 lb., especially for the ends and the top, or for the first chamber of a set.

This thickness is sufficient for a chamber to last ten years; the bottom lasts longest, just because it does not get so hot as the sides and the top, and because it is more protected by the mud of lead sulphate which collects upon it; only in cases of gross neglect (for instance, if nitric acid gets to it) it is quickly worn out, whether the lead be thick or thin.

The sheets of lead were at first joined together by the ordinary soft solder, which is very convenient for use, but is soon corroded by the acid. Places soldered thus are also much more brittle than pure lead. So long as the chambers had to be put together in this way, there was occasion for innumerable repairs.

Another plan (which is much better in this respect, but takes much lead, and is only easily applicable for straight seams) is the *rabbit*-joint. The edges of two sheets of lead are turned over in the way shown in fig. 109, put into one another, and beaten down on a smooth surface. Such joints are gas-tight, and have

Fig. 109.



been used here and there in England till within the last few years.

The kind of joint now generally used is that made by *burning*, with the lead itself—that is, by melting it with a hydrogen flame fed by compressed air. In this way the two sheets are joined so tightly, that with good work the joint, being thicker than the sheets, is actually stronger than they. If the work is rough and uneven, foreign substances will easily be deposited in the rough parts, by which the lead may be damaged.

This mode of joining was invented by Debassyns de Richemont. Two apparatus are required for this, whose construction is shown in figs. 110 and 111. Fig. 110 shows the "plumbers' machine"—that is, the hydrogen-apparatus—quite similar to an ordinary laboratory gas-holder, but made of lead, often with a wood casing. The lower vessel, A, contains a lead grating, K L, upon which granulated or scrap zinc is put. The upper vessel contains dilute sulphuric acid. The connecting-tube with a cock *f* allows the gas to pass out of the opening C, after it has first got washed in a water-vessel. Often there is a plain outlet just above the cock *f*. The outlet is connected with a long india-rubber tube, by means of which the gas can be conducted to a distance. The

Fig. 110.

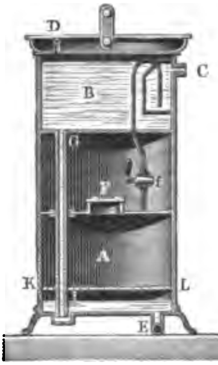
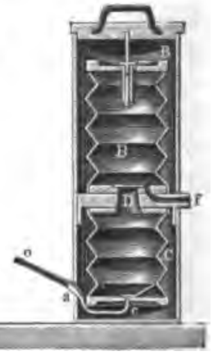


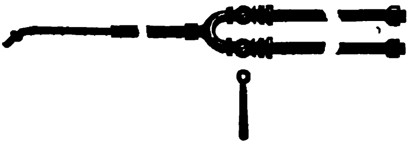
Fig. 111.



tube G serves for running sulphuric acid from B to A. It can only run in as gas is allowed to escape by opening the cock *f*; and thus a continuous current of gas is obtained. The openings D, E, and F serve for introducing acid and zinc, and for running off the solution of zinc sulphate.

The second part of the apparatus, which is shown in fig. 111, is simply a portable smith's-bellows of cylindrical shape, the lever of which, *o a c*, a boy works with his foot. The air is forced through the valve D from C to the closed air-vessel B, and escapes through the opening *f*, likewise connected with a long elastic tube. The two tubes are united by the blow-pipe, fig. 112; and the mixture is ignited. Each limb of the blow-pipe is provided with a stop-cock, by turning which the plumber may admit more air or hydrogen at will, and thus can produce a flame of any size, which, however, should never be an oxidizing one.

Fig. 112.



The mouth-piece of the blow-pipe itself is sometimes connected with the fork-shaped piece by a short elastic tube, to make it more mobile. Besides the ordinary mouth-piece, ending in an aperture of about $\frac{1}{25}$ of an inch diameter, the plumber also carries another, provided with a small brass shield, to obtain a steady flame in windy weather. The gases unite only immediately before escaping; and thus the flame cannot strike back. By means of this machine a pointed and very hot hydrogen flame is produced, which, at the place where it touches, melts the lead immediately down to a certain depth; and the art of burning consists in touching and melting parts of two sheets *at the same time*, which, on cooling, solidify to a whole.

It has happened that plumbers have been poisoned by arseniuretted hydrogen, produced by impurities in either the zinc or the sulphuric acid. The hydrogen can be freed from this by washing it in a solution of cupric sulphate, by which the arsenic is precipitated.

The *burning* itself is a kind of work requiring much practice, because the plumber must not allow the flame to act a moment too short a time or too long. If he does the former, the fusion is not perfect, and the seam is not tight; if he does the latter, he burns hole in the lead. Wherever it is possible, one sheet is laid about 2 inches over the edge of the other, as shown in fig. 113. The seam is made with the help of a strip of lead, about $\frac{5}{8}$ by $\frac{1}{4}$ inch thick, which the plumber holds in one hand whilst he guides the blow-pipe with the other. He works in this way:—He touches with the flame the place *a* (fig. 113), where the edge of one sheet lies upon the other, so that the surface of the lead (previously scraped clean) just melts, but the back part of the lead does not melt. At the same time he holds the above-mentioned strip in the flame, so that drops fall from it onto the just-melted part of the sheets, and the whole is united into a seam, *b*, all fusing together into one mass. By a slight motion of the wrist the plumber removes the flame for a moment, and the lead, which has only just been melted, at once solidifies; in another second the flame is again directed upon the lead, and a new drop flows partly over the first one; so that at last the whole seam takes the shape shown in fig. 114.

Fig. 113.

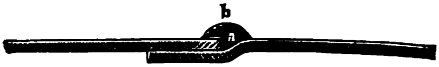
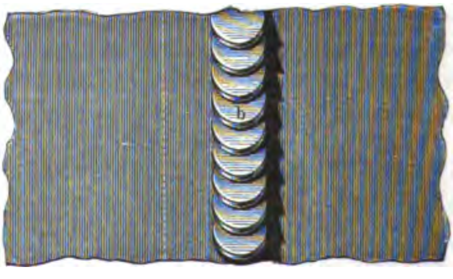


Fig. 114.



Although all this is much more easily described than carried out successfully, still the burning of *horizontal* seams is learned in a comparatively short time, and can be done very quickly by a practised workman.

The burning of *perpendicular* (upright) joints is much more difficult, and, even in the hands of the most experienced workman, takes at least three times as much time for the same length of seam as horizontal burning, without ever being as strong as the latter. This is easily understood; for the melted lead, which quietly remains lying on a horizontal sheet, in upright burning at once runs down; and this can only be prevented in one way: the lead must be heated exactly up to the melting-point, and the flame instantly removed till the seam has solidified; and the burning must always be done from the bottom upwards, so that to a certain extent the seam will retain the drops of lead. In this case much use cannot be made of strips of lead for strengthening the seam.

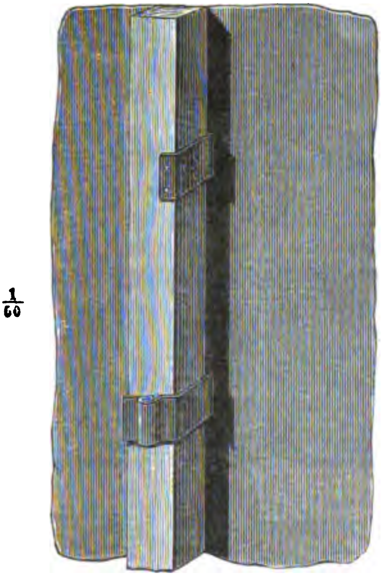
A practised plumber can burn as much as 10 feet upright or 25 feet horizontal joints in an hour; but such figures are only reached in piece-work.

The way of building a lead chamber in England is usually as follows:—The commencement is made with the sides, for which the sheets are made as wide as possible (most lead-rolling mills supply them up to 7 feet 9 inches, some even wider), and so long that they extend 4 inches beyond the height of the chamber, of course taking into account that one side of the chamber is a foot higher than the other. 6 inches are reckoned to turn over the crown-tree; but 2 inches are saved at the bottom, because the lead afterwards expands by the heat of the chamber.

Now, on the wooden floor before mentioned a wooden table (the "sheet-board") is constructed, held together at the back by battens, but completely smooth on the upper surface. It has the width of two or three sheets of lead (that is, 15 feet 6 inches, or 23 feet 3 inches), and the height of the chamber—which, of course, can only be done when (as is generally the case) the chamber is at least as wide as it is high. On this table the sheets of lead are rolled out flat, placed side by side, so that one overlaps the other 2 inches, and burned together; at the same time all the straps (of which we shall speak directly) are burnt to the lead, which can be done because the upper surface will afterwards be the outer one. The upper edge is bent round the sheet-board, so as to hold it fast; and when every thing is finished this end is wound up by a set of pulleys, so that the sheet-board is raised along with the sheets of lead, and lies flat against one side of the chamber-frame. Now the upper edge of the lead is at once bent over the crown-tree and nailed down, as well as all the straps. For this no cut or wire nails are ever used, but wrought nails with broad heads ("plate-nails"), about 1½ inch long, whose heads are all protected against the acid by dipping a few at a time into melted lead. When the lead has been completely fastened to the frame, the sheet-board is lowered down, moved forward its own width, and another piece of the chamber-side made upon it, till in this way the chamber-sides and ends have been finished all round. Only in the corners it is preferable to use single sheets, which form a rounded corner; this is much stronger than a sharp edge. The object of the described process is this, to reduce the upright burning to a minimum. It is much better than the former plan of hoisting up each single sheet, turning its margin over the crown-tree, and unrolling the sheet by its own weight. In this case every single sheet had to be joined to its neighbour by upright burning, and the straps had to be burnt on in an equally inconvenient manner. If at all possible, the seams ought not to be behind the uprights, so as to be better accessible for repairs; and for this reason also it is to be recommended to make the chamber-frame as shown in fig. 107, where the uprights do not touch the lead at all.

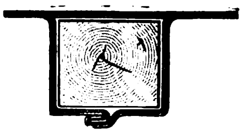
The *straps of the sides* must be arranged according to the style of the frame. If this only consists of uprights mortised into the crown- and sole-trees, without any cross rails, the straps consist of perpendicular pieces of lead, nailed sideways to the uprights with five leaded nails each. The strap ought to be long enough to turn over the edge of the upright, so that two of the nails come to the front (fig. 115, upper part). Such straps are placed alternately on one and on the other side of the upright, one about every 4 feet. These straps do not allow the chamber-lead to follow the changes of temperature by extension or contraction. This easily leads to deformation of the sides and tearing off of the straps; and it is therefore better to avoid this style, which can be done by only nailing down the top strap in this way. For the lower straps longer pieces of lead are burnt to each side of the upright, which meet on its front, and are there joined by rabbeting (see fig. 115, lower part, and fig. 116). There are no nails used here; so that the lead walls may move up and down the upright, whilst at the same time they are all the more stiffened by being held fast in two places. This, of course, takes more lead and labour than simple straps. In each case the straps are about 8 inches in depth. If the frame is provided

Fig. 115.



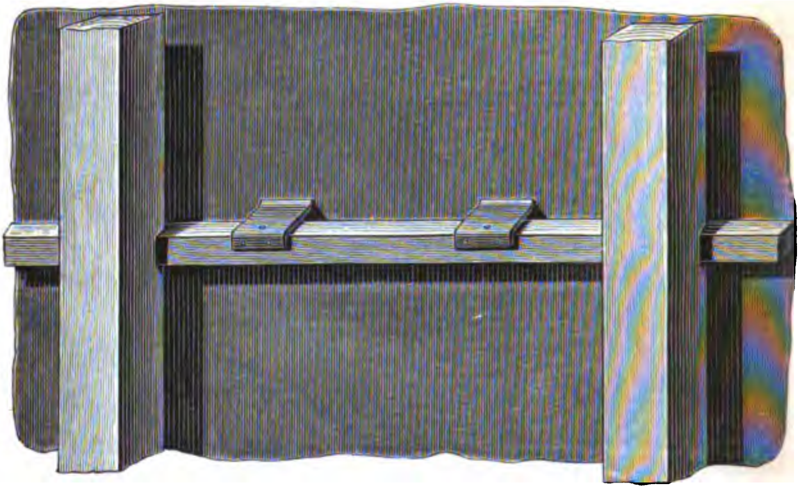
with horizontal cross rails, there are only a few upright straps used—sometimes none, only horizontal ones, turned down over the rail, and nailed to it (fig. 117), two of 6 inches length for each rail. This style of straps protects the chamber-sides much better against deformation than the upright straps, and carries the weight better upon the frame; it also permits the lead to be kept further apart from the wood, since the straps may leave about ½ inch (not more) space between the lead and the rails. The diagram shows this

Fig. 116.



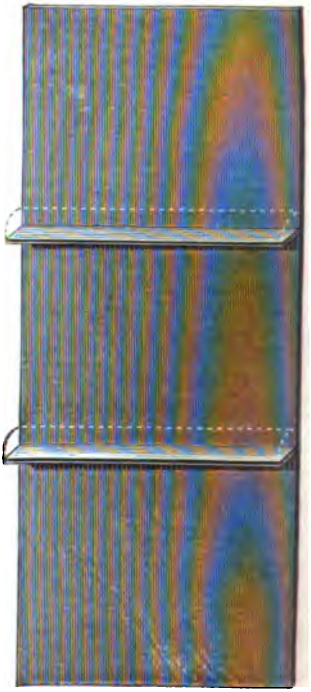
The chamber-sides can also (as at the Thann Works) be made of horizontally disposed sheets of lead. The overlap in this case is nailed to the horizontal cross rails in lieu of straps, as shown in fig. 118; but first the whole height of the chamber-side is finished, the whole is rolled upon a wooden roller, and allowed to unwind itself by its own weight from the top. In this way there is not so much pull upon the seams as if the chamber were made of sheets hanging down by their length, since each sheet is supported just in the place where there would be a pull. This plan, indeed, seems

Fig. 117.



to be worthy of general recommendation; for it saves the lead and labour of all the straps, and supports the chamber very well.

Fig. 118.



At least as substantial is the plan used at Aussig. There are no side-straps at all; but to each upright of the frame corresponds a strip of lead burnt to the chamber-side along its whole height, probably the lap turned outside. This is nailed sideways to the upright. Between this and the lead there is a wooden lath, to increase the contact of air with the chamber-lead as much as possible. Fig. 119 shows this in horizontal section.

In the first-described case, now generally used in England, at first only about a yard of the seams is burned, and that at the top, so that the chamber can be covered in and the remainder can be done at leisure in bad weather The next thing, therefore, is the *chamber-top*. For this we need a temporary scaffolding, movable on wooden rollers, made of high trestles joined together at the top, equal in height and width to the chamber, and in length to at least two (or, better, three) sheets of lead. This scaffold is put together within the chamber itself, its separate parts being got in by bending back one of the side sheets. It is covered on the top with a flooring of boards; and upon this the sheets serving for the chamber-top are flattened out. These are a little wider than the chamber, so that they project 3 inches on each side. Thus they do not project quite as far as the overlap of the side-sheets (6 inches), and there remains a joint suitable for burning (fig. 120, *a*), which is burned very strongly. Now the sheets themselves are joined by burning, and all the top-straps are burnt on. The latter serve for fixing the chamber-top from above to the top joists carrying it. The latter, for a chamber 20 to 26 feet wide, are 3 to 4½ inches thick and 10 to 12 inches high, and are placed at distances of 14 to 18 inches from centre to centre. Their length is at least sufficient to reach to the outside of the

Fig. 119.

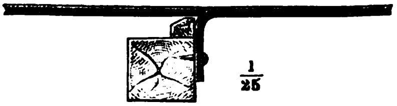
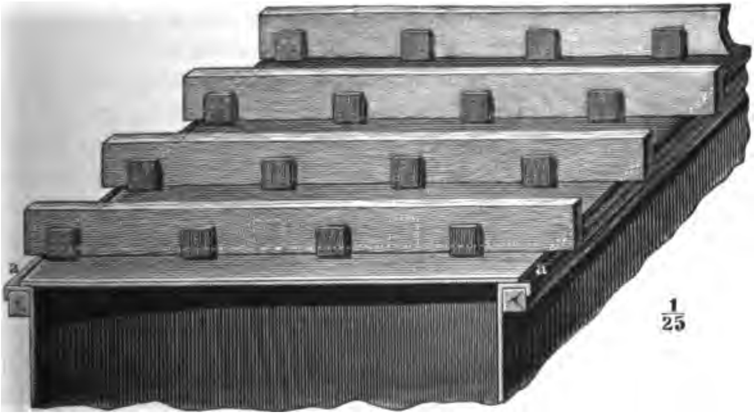


Fig. 120.



crown-trees; it is better if they even project a little beyond, to have a good support. The straps themselves are made 7 inches square, and stand alternately on both sides of the top joists, about 3 feet apart on each side. At other works there are fewer but longer straps. They are bent up and nailed to the top joists laid above them on edge, with five leaded nails each. When all this has been done, the top joists, by the help of the straps, carry the lead of the chamber-top, and the joists themselves rest upon the side frames, but separated from them by the overlap of the chamber-sides.

The top joists are protected from canting over by a few boards nailed across them, which at the same time serve as a passage on the chamber-top. Where the chambers are roofed in, mostly longitudinal sleepers are laid on the top, joined to the top joists by iron clamps, and the whole suspended from the timber of the roof, which must be made strong enough for this purpose; but it would appear that even with roofed-in chambers it is safer to keep the chamber-top independent of any movement of the roof.

Where the chamber is too wide for any single cross joists, two lengths of these must be joined together and trussed, according to the rules of carpentry; in this case trussed girders may run across the width of the chamber, and the proper joists, to which the top lead is fastened by straps, run parallel with the long sides of the chambers; they are either morticed into the girders, or (which is the stronger plan) they rest in cast-iron shoes bolted to the girders. This, however, is only required for chambers standing in the open air; it is not very convenient, as the side frames have to be weighted very much. Such wide chambers, as we shall see below, have not altogether turned out well.

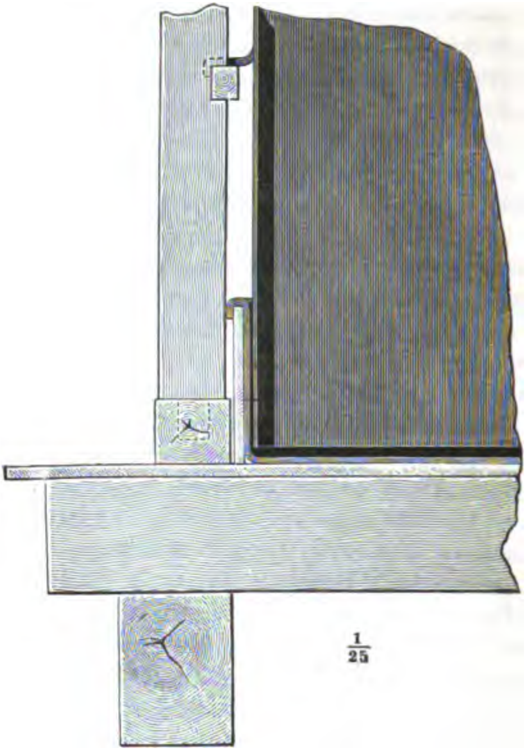
Quite different from the just-described chamber-tops are those found in some continental works. There are no wooden top joists, but, in the place of these, thin iron rods about ½ in. thick, fastened to the chamber-top by a lead covering burnt on each side to the chamber-lead. These horizontal rods themselves are suspended from the roofing by means of ¼-inch rods placed at short distances from each other. This system cannot be employed at all for chambers standing in the open air.

The *chamber-bottom* is left to the last; and it happens no doubt very rarely (in England probably never) that, according to older prescriptions, the bottom is laid down first and protected by straw and boards while the remainder of the chamber is being made. It is, on the contrary, made last of all, but not always in the same way. In some works the side sheets are burned to it all round, and openings are left in a few places for drawing off the acid, for taking samples, &c. In the great majority of works the bottom is independent of the sides, and forms an enormous tank with turned-up sides, into which the chamber-sides hang down, dipping into the bottom-acid, and thus forming a hydraulic joint. This allows the chamber-sides to expand and contract with the temperature, and also makes the bottom-acid accessible from all sides, so that it is preferred in spite of the larger expenditure of lead. Often the upstand, which ought not to be less than 14 inches high, so as to afford a good deal of room for acid, is made from a narrow sheet of lead of double width, by bending up one half and leaving the other half to form a portion of the chamber-bottom; the latter is then finished by burning it together with other sheets of lead. This is more convenient for the plumber than taking sheets equal in length to the width of the chamber, along with the height of the upstand on each side. The latter must not be left loose, because it is easily bagged out by the side pressure of the acid; but a 1-inch board is placed all round the chamber-floor, over the edge of which the upstand is turned round and nailed down. This is shown in fig. 121.

In some works the bottom is divided into two, three, or four parts by partitions of the whole height of the upstand. The object of this is, not to empty the whole chamber in the case of repairs; but it is very rarely done, as this arrangement prevents a free circulation of the acid, and as the bottom mostly suffers less than any other part of the chamber—excepting through gross neglect, by the formation of nitric acid, which ought not to happen at all.

In England, where the winters are not severe, lead chambers are hardly ever roofed in, but are only built so that the rain-water can run off as described above. But even then the space between each two chambers must be covered by a light roof, and the whole set must be surrounded by a wooden shed, because a gale might tear the lead off the frames, or even throw down a chamber altogether. These wooden houses have windows or Venetian blinds, changed according to the wind. In windy places they are always made first, as soon as the foundations and the frame are

Fig. 121.



finished, but before the lead has been fastened to the latter, because during the building the incomplete chamber is even more exposed to being thrown down by a gale than after completion.

Thus the chamber-tops are exposed in England to the heat of the sun in summer and to the snow in winter; this is possible because neither of them occurs to an excessive degree. In the less windy places even the chamber-sides are sometimes left without protection against the weather, but never so in well-arranged works. In the south of France, on the other hand, the chamber-tops are always protected against the sun and the rain by a roof; but the sides are always exposed, which, on account of the heat of the sun there, is certainly very wrong. In the north of France, in

Belgium, and in Germany the chambers are always completely enclosed in buildings, usually of a very light construction.

We must now say something of the *renewal of the chambers.* In a set of chambers the greatest wear and tear is experienced by the first chamber; and this is consequently sometimes made of stronger lead, say 7-lb., to last as long as the others, made of 6-lb. lead. A chamber will last very much longer if the frame be made substantial, and the straps be well burnt on and nailed down and numerous enough, so that they will not be readily torn off. Should this happen, the mischief must be repaired at once: nowhere does the saying come more true "that a stitch in time saves nine." If the repair is put off too long, the chamber-lead, pulled by its own weight, wrinkles irregularly, and the chamber becomes unfit for work much too soon. Especially those parts of the frame most exposed to the action of the acid must be carefully looked after, and, in case of need, at once repaired, before the parts of the lead sides dependent upon them have lost their support and have collapsed. This is most necessary at the junctions of connecting-pipes, at the places where the acid is siphoned off, &c. The wind must also be kept off, and any loose pieces in the bratticing round and between the chambers promptly put right; a gale of wind may tear off the straps of a whole chamber-side at once, or force the frame to one side. The gangway round the chambers ought to be wide enough (say 5 feet) to admit of easy control and repair.

In normal circumstances a chamber will generally last from eight to ten years, but with many repairs during the latter years. In the case of chambers without a roof over them the top generally wears out first, then the parts dipping into the bottom-acid and the ends; the bottom remains good up to the last, unless nitric acid gets to it, which most easily happens in the last chamber, if its strength is allowed to run down too much.

When a chamber requires so much repairing and patching that it does not seem likely to pay, and when, after all, the escape of the gas from the too numerous chinks and rents can no longer be kept down, it is very bad economy not to pull it down at once; for the yield of acid must fall off very much. In this case a temporary connexion is made between the two apparatus on either side of it, the acid contained in the chamber is worked down as long as it will run, a hole is cut into its side, and men provided with india-rubber boots are sent in to shovel up the *mud* lying at the bottom into a heap, from which a good deal of acid is still obtained by draining. The mud must now be removed; if the space underneath is free, a receptacle is formed by low banks of clay, a hole is cut in the chamber-bottom, and the mud pushed down. If this is not possible, it must be removed in a much more troublesome manner, by thickening it with sawdust and washing with water. In either case it is dried in a reverberatory furnace, sometimes with the addition of a little lime in order to prevent the escape of acid vapours. For all that, this operation usually causes a very disagreeable stench, probably owing to arsenic, selenium, &c. The dried mud, principally consisting of lead sulphate, is either smelted for lead in a small cupola heated by coke, or simply sold to the lead-workers.

After taking out the lead-mud, the chamber-lead is detached from the frame, and the good whole pieces rolled up for use as sheet lead; the others are melted in an iron boiler, the dross is scummed off, and the lead cast in the usual pig-moulds; at the lead-rolling mills this lead is very well liked for other chemical purposes (see p. 42). Counting up the pig-lead, the dross, and the lead sulphate, nine tenths or upwards of the original weight of the chamber is recovered; the remainder has gone away in one shape or another with the vitriol made.

If the frame has been substantially made, it stands a second, sometimes a third lead chamber, with a few repairs, putting in odd beams &c. Of course, in case of any doubt, it would be extremely bad economy to run the risk of having to stop a chamber because its frame would not hold out as long as the lead.

The *size of the chambers* varies very much. Apart from the "tambours" of the French system, the proper chambers are made with as little as 10,000 and as much as 140,000 cubic feet capacity. Such small chambers are no longer built as main chambers; the usual capacity of these may now be taken as ranging from 25,000 to 70,000 cubic feet, more frequently nearer the upper than the lower limit. Smaller chambers cost much more, comparatively, than large ones, and do not afford any corresponding advantages.

About the *shape* of the chambers there is not much diversity of opinion now. In some places they were made almost of a cubical shape to save lead; and there are such of 60 feet width and almost as high. But this both causes some difficulties in constructing the wood frame, and, what is worse, the gases are mixed too incompletely in such a large space, and, as a matter of fact, the yield of acid is too small. Cubical chambers are laid out new hardly anywhere now.

On the other hand, many acid-makers formerly started with the idea that the production of vitriol in a chamber is a process of *condensation*, and that it could be promoted by enlarging the surface, as in other similar processes. This was a totally wrong idea. In a real condensing-process the vapour of a substance must be condensed to a liquid by contact with cooling surfaces; but in the chamber process the vitriol cannot from the first exist in the form of vapour, the temperature being much too low for that; it must at once be formed as a liquid, and fall to the bottom in the shape of rain; and this will be the case all over the chamber, in the centre no less than close to the sides : this has been confirmed by direct observation.

Formerly, before this was well understood by all acid-makers, they strove to enlarge the surfaces, and they sometimes reared costly and complicated structures, such as glass partitions, inside the chambers, which mostly collapsed very soon without its being known (see below).

An arrangement of Ward's (Richardson and Watts, vol. v. p. 213) consists in a kind of mixing-chamber, for the combustion of 7 tons pyrites in twenty-four hours, 64 feet long, 16 feet high, and 20 feet wide, followed by a second lead chamber, or flue, 200 feet long by 3 feet high and 3 feet wide, almost filled up with sheets of glass to a length of 25 feet. The sheets lie in a horizontal position, and are kept a little apart by strips of glass, to permit the passage of the gases. Ward believed that upon these sheets (in lieu of which tubes might be used) nitrous vitriol would condense and afford a large surface to sulphurous acid. His plan does not appear to have been very successful.

A similar principle underlies the proposal made by Gossage and many others, and frequently carried out in practice, of filling the chambers partially or entirely with coke, or of erecting special coke-towers at the end of the set, in order to cause a better mixture and mutual reaction of the gases. Of course, this was meant to save chamber space; otherwise the coke would have no object, and could only cause the acid to become impure. But apparently this object has not been attained; no chamber space is saved; and at some works, where the chambers had been filled with coke, it has been removed again. Certainly, before the general introduction of the Gay-Lussac tower, many works had a lead tower built between the last chamber and the chimney, or in lieu of the latter; these towers were 3 feet or more in width, and from 10 to 30 feet high; they were filled with coke and moistened by a small jet of water or of steam. The idea, however, was mostly only that of retaining any sulphuric acid carried away mechanically.

The same erroneous principle of surface condensation is at the bottom of Hemptinne's chamber-system, which will be described afterwards in connexion with his system of concentrating. Also the apparatus of Verstraet (Bull. Soc. d'encourag. 1865, p. 531), which was worked in Paris for some time, but had to be given up as impracticable. It consisted of a number of stoneware jars without a bottom, covered 430 square feet of ground, cost only £280, and was to supply daily a ton of vitriol of 106° Tw. There were twelve perpendicular stacks of five jars each, filled with coke and traversed by the burner-gas; nitric acid ran down over one of them, meeting the sulphurous-acid gas; and the resulting acid was in regular rotation run over the other stacks.

The apparatus of Lardani and Susini (Bull. Soc. Chim. viii. p. 295) is founded on the same principle. Its peculiarity is a "reaction-apparatus," whose lower part is filled with sulphuric acid, on the top of which a thick layer of nitric acid is floating; the upper part, divided from the lower by a perforated partition, is filled with pumice; the nitre-gas is regenerated to nitric acid by an excess of air and water in a system of pipes filled with pumice or coke.

Certainly the gases within the chamber must have an opportunity of thoroughly *mixing*; and the usual shape of the chambers answers for this. They are usually made of a moderate height and width, say 16 to 21 feet high and 19 to 26 feet wide, but very long—100, 200, or even 330 feet long. Hasenclever has chambers 33 feet wide and high and 130 feet long. The gas entering at one end and leaving at the other must travel along the whole length of the chamber, and thus get thoroughly mixed; the reactions are to take place so completely that at the end no more SO_2 is left. Usually, at any rate in larger works, the whole space is divided into several chambers; but this is not necessarily the case, and good results are also obtained with a single chamber, if it be made sufficiently long.

An author already quoted several times, H. A. Smith, in a pamphlet on the chemistry of sulphuric acid-manufacture (a German translation of which, with many valuable additions, was published by Bode in 1874), has tried to prove that thus far the process going on inside the acid-chambers has been misinterpreted, that sulphuric acid is essentially formed only at a height of 3 to 6 or at most 8 feet, and that the whole space above this only serves as a reservoir for the gas, in which no reactions take place. Smith has inferred this partly from observations of temperatures, starting from an assumption contrary to the ordinary opinion, and not at all proved by himself, viz. that the most favourable temperature for the formation of sulphuric acid is 200° F. (=94° C.). He made only *two* experiments, and those of the roughest kind, on the influence of temperature on the formation of sulphuric acid, judging exclusively from the occurrence and the vanishing of the red vapours, which does not prevent him from positively stating the above conclusion. Now he made a number of experiments with thermometers fixed at the following heights over the chamber-bottom, viz.:—first, 24 feet; second, 15 feet; third, 8 feet; fourth, 3 feet. The *first* and *second* were found pretty constantly = 130° F. (=54°·4 C.)—that is, *the temperature most favourable to the formation of sulphuric acid*, according to all other opinions; and yet, on the strength of the above-mentioned two rough experiments, unsupported by any other evidence, he concludes that this portion of the lead chambers does not serve as a "condensing-space," but merely as a reservoir for the gases. At the third height (8 feet) he finds such unequal and anomalous temperatures that it is inconceivable why even this height is considered a "condensing-space;" and only at a height of 3 feet above the bottom does the temperature, in *one half* of the chamber, approach his normal temperature of 93°·3 C., but suddenly falls again ultimately to 48°·9 C. Still this does not disturb Smith in holding to his idea (entirely evolved out of his inner consciousness) that 93°·3 C. is the normal temperature for the process of sulphuric-acid-making, and that this temperature only occurs at a low elevation above the chamber-bottom. That Schwarzenberg's observations of temperatures (to be quoted below) directly contradict his own, probably remained unknown to him, although Schwarzenberg's work appeared four years before Smith's pamphlet. The author's own information likewise proves that the temperatures near the top of the chambers are higher than those near the bottom, in direct opposition to Smith's assertions.

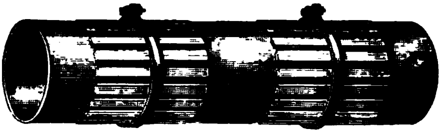
Another kind of argumentation attempted by Smith is still more faulty, viz. that founded on the quantity of vitriol formed at different heights of the chamber. He has fallen into a curious error, first publicly pointed out by Hasenclever in Hofmann's 'Bericht,' i. p. 179, but previously noticed by many readers of Smith's pamphlet. Smith placed two collecting-dishes for acid, one 4 feet, the other 16 feet above the chamber-bottom. After nine days he found that the acid in the upper dish had only increased by $\frac{1}{16}$ inch, whilst in the lower dish a copious and regular formation of sulphuric acid had taken place. But here he overlooks that the acid formed in the chamber falls to the bottom, and that consequently a dish placed near the bottom receives not merely the vitriol formed immediately above it, but all that formed in the whole of the chamber-space perpendicularly over it; thus it must always show all the more acid the lower it is placed. But even according to Smith himself, at 18 feet above the bottom there was still a copious formation of sulphuric acid.

The strongest refutation of Smith's theory is afforded by his own estimations of sulphurous acid in the gas. Here the source of error just mentioned could not occur; and, in fact, we find that at 40 feet from the entrance of the gases the mixture is almost perfect, and that the percentages of the chamber-gas at 3 feet and 15 feet above the chamber-bottom are almost exactly alike, whilst, according to Smith's theory, near the bottom much less SO_2 ought to be found than near the top. The differences between the two curves on p. 39 (we always quote the pages of the German edition) are very slight. A similar proportion occurs in the case of nitre-gas; but of this there is nearly always even more found at 3 feet than at 15 feet above the bottom. None of these glaring facts disturb Smith's confidence in his preconceived ideas; he asserts that the chambers must be divided into a working-space and a reservoir for the gas, and that the latter may be left out as useless. As the most suitable form of a chamber he states a length of 150 feet, a width of 25–30 feet, and a height of 10–12 feet, although the logical conclusion from his own, certainly most arbitrary, premises would be that the chambers ought not to be above 4 feet high. This, however, he has not ventured to propose. Smith's assertions have been directly refuted by Hasenclever (*l. c.* p. 178), who fixed lead dishes in several places of the chamber, covering them over at a distance of a foot, and who thus found that about the same quantity of sulphuric acid was formed all over the chamber. Hasenclever concludes from this that within certain limits that chamber is the best which, for a given cubic space, requires the smallest surface of lead, and he goes up to 33 feet width and height in his chambers. This, however, seems too much, and is contradicted by many years' experience at the Oker Works (Bräuning, Preuss. Zeitschr. 1877, p. 136), where 16⅔ feet width and height have been found to be the most suitable size for utilizing the chamber-space.

According to Bode (Dingl. Journ. ccxvii. p. 312), Smith's statements have been refuted in even a more direct way. At the Oker Works a set of chambers was erected according to his proposals; but it was found that it produced vitriol not in the ratio of its *area*, as had been assumed, but in that of its *cubical contents*, so that the erection of these low chambers meant a waste of lead, carpentry, ground-space, and roofing. Bode considers that the "surface theory" has accordingly been completely exploded.

Thus far we have spoken as if only *one* chamber were working; and, in fact, frequently this is the case. Scheurer-Kestner (Wurtz, Dict. iii. p. 147) mentions a single chamber of 142,000 cubic feet capacity, and quotes the experience of several works, according to which it is quite unnecessary to divide the set into several chambers. Much more usually, however, several chambers are combined to form a set, which affords this advantage —that for repairs it is not necessary to stop the whole set. The single chambers are connected by round pipes or angular flues (tunnels). The former are preferable, because they can be made without a frame, and because they stand better. They must, however, be made of strong lead, say 9 to 12 lb. per square foot, and bound here and there with iron hoops, between which and the lead wooden staves are placed in order to keep the pipes in shape; but if the weight of the lead amounts to 15 lb. per square foot, no staves are needed. Fig. 122 will make this clearer.

Fig. 122.



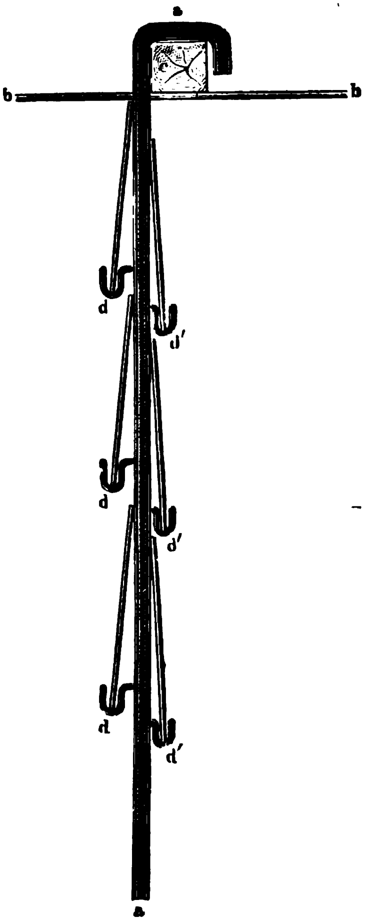
The iron hoops serve also for suspending the pipes from beams &c. The *width* of the pipe introducing the gas into the first chamber, whether it comes from the Glover tower or from the burners, must be adapted to the quantity of gas conveyed. For a combustion of 7 tons pyrites daily a pipe of 2 feet diameter, for 9 tons one of 2½ feet, upwards of that one of 3 feet diameter will do; more than 10 tons are rarely consumed for a single set in twenty-four hours. Since the volume of the gas decreases in its onward journey, the connecting-pipes between the single chambers may be successively a little smaller; but it is not well to grudge any thing here, since no harm is done if the pipes are too large, but very much if they are too small.

A great diversity of opinions exists upon the point how the single chambers are to be *combined to form sets*. Among the hundreds of vitriol-works very few will be exactly alike in this respect; and frequently even in the same works different combinations are found. We may, however, consider it as established that it is almost indifferent in which way the chambers are combined, if they are, in the first instance, properly built (that is, not too high or wide), and if, secondly, they possess a certain cubical capacity for the quantity of sulphur or pyrites to be consumed. Within these limits those combinations are best which require least lead, and which are laid out so as to afford the greatest facility for supervision. Of course there is also an ultimate limit to the capacity of the whole set; but opinions differ upon this point also. At some works a set consists of nine or eleven chambers of 35,000 cubic feet each; at others, equally large, it is limited to three chambers of 42,500 cubic feet each, &c. Thus at Hebburn-on-Tyne there are several sets of three chambers each, each of them 20 feet wide, 125 feet long, 17 feet high on one side, 18 feet on the other side; each set serves for 18 burners, burning 7 cwt. daily. At Gateshead there are several sets of three large chambers, each so arranged that two of them communicate separately with a set of kilns ("working-chambers"), and both of them are connected with the third chamber; the whole set has a capacity of about 200,000 cubic feet. More usually the gas passes through all three chambers in succession. Very often four chambers are combined, each of them about 20 x 20 x 130 feet,—or five chambers, two of them working-chambers, thus, $\begin{matrix}1-3\\2-4\end{matrix}\!\!>5$,—or even six chambers, thus, $\begin{matrix}1-3\\2-4\end{matrix}\!\!>5-6$.

On the whole it is not advisable to combine too many chambers and to make the sets too large, certainly not above 200,000 cubic feet; otherwise all the connexions &c. must be too large, the first chamber becomes too hot, and any disturbances of the process are felt over too large an area. On the other hand, a set of less than, say, 130,000 cubic feet takes as much labour and auxiliary apparatus as a larger one, and will thus be more expensive. In a larger set any disturbances in the nitre, steam, draught, &c. are found out before the gas has got to the outlet, and thus can be more easily put right.

At Uetikon, near Zurich, there is a peculiar kind of chambers. Each set only consists of one large chamber, 330 feet long; within this, however, there are two partitions, dividing it really into three chambers. The partitions are made as shown in fig. 123. A row of perpendicular

Fig. 123.



iron gas-tubes of 1-inch bore, covered with lead, *a*, is placed across the chamber, carried through its top, *b*, and hung from one of the joists *c*. At vertical distances of 2 feet there are lead hooks, *d d*, attached to the tubes, on the other side other hooks, *d′ d′*, a little lower. On these sheets of glass 2 feet × 2 feet 6 in. are placed loosely, leaving chinks of about 1 inch width for the passage of the gases, in order to mix them better. These partitions do not seem to offer any guarantee of durability; and it is a fact that at other works, formerly possessing similar glass partitions, they have been removed again; sometimes they are said to have suddenly collapsed and cut through the chamber-bottom.

The simplest kind of internal partition, a lead one, is not practicable, because the lead, exposed to the heat and the gas on both sides, is very quickly worn away.

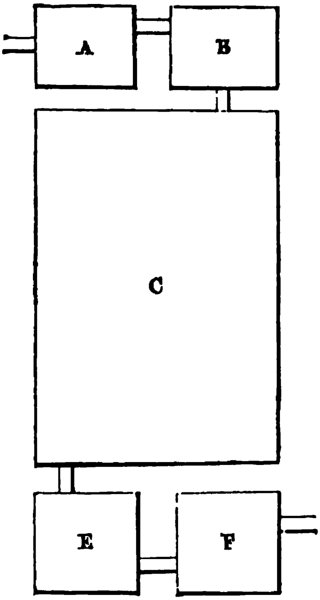
The different chambers of a set are either placed on the same level, or, more suitably, each following chamber is placed 1 or 2 or, better, 3 inches higher than the preceding one, so that the acid of the back chambers can be run more easily into the working-chamber. In this first chamber the acid is both strongest and most free from nitre; and it is therefore preferable to draw off any acid from this, whether it be for sale, for use, or for concentration. The acid drawn off is replaced partly by that newly formed in the same chamber, partly by the weaker acid run over from the other chamber. If there is only one long chamber, the acid is always found strongest near the entrance of the gas.

In England, mostly, all the chambers of a set are of equal size, apart from local circumstances; and this plan is now more frequently found on the Continent as well than formerly, when the French system, even now the more usual one, was the only one to be met with. In this system there is a "large chamber," C, fig. 124, placed at the lowest level, combined with a few small chambers at a higher level, both before and behind the large one. Thus the first small chamber or "*tambour*," A, serves for denitrating the nitrous vitriol by hot water; the second one, B, for introducing fresh nitric acid; the third and fourth tambours, E and F, for finishing the reaction.

In the south of France (Favre, 'Monit. Scient.' 1876, p. 272) there is mostly a large chamber of 135 × 26 × 20 feet, or of 100 × 16 × 22 feet, combined with two small chambers, together about 140,000 cubic feet. At Aussig each large chamber is

200 feet long and 24 feet wide, and is combined with a small tambour for catching the fine dust, and two small end chambers, not receiving any steam, but only serving for cooling the gas previously to its entering the Gay-Lussac tower. The system considered the best at Oker (Bräuning, p. 136) is the following:—two tambours of 127 and 106 cub. metres, one main chamber of 1459 cub. metres, one back chamber (not fed with steam) of 162 cub. metres; total 1854 cub. metres. All the chambers are 17 feet wide and high; the main-chamber bottom is divided by partitions of 3 feet 3 inches height into 5 compartments. The connecting pipes are 18 inches wide; they introduce the gas at $\frac{2}{3}$ of the height, and take it away at $\frac{1}{3}$ of the height.

Fig. 124.



Some manufacturers reject all preliminary chambers, because the chamber process is carried on best if a large space is afforded at once for the mutual reaction of the gases. Thus in a large French works two thirds of the whole chamber-space are occupied by the first chamber, two ninths by the second, and one ninth by the third.

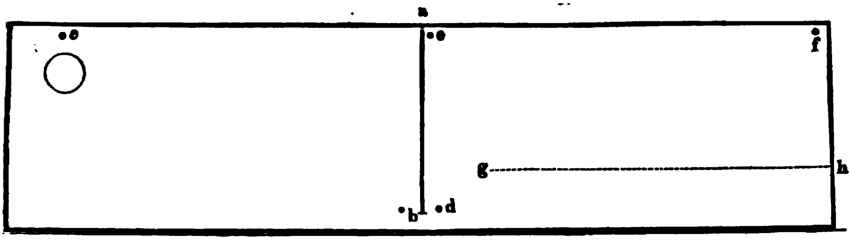
On the whole, small chambers seem objectionable, because they require more lead and space than large ones of equal capacity. A preliminary chamber, however, is serviceable, where no Glover tower is present, for catching the dust and cooling the gas, so as to save the large chamber. For the same reason the nitric acid is usually introduced into a special tambour; but it is best, as we shall see, to run it down the Glover tower.

The waste of lead in small chambers is more easily seen in a definite example. A chamber of 100 × 20 × 20 feet has a cubical capacity of 40,000 cubic feet and a surface of 8800 square feet. A tambour of 16 × 10 × 10 feet has a capacity of 1600 cubic feet and a surface of 840 square feet. Its contents are therefore $\frac{1}{25}$, but its surface almost $\frac{1}{10}$ of that of the large chamber; and consequently its surface is nearly 2½ times as large, in comparison with its capacity, as that of the large chamber.

On the other hand the saving of lead may be carried too far: if chambers are too high and wide, the gas is not properly mixed; and if they are excessively long, they cannot be supplied by a single jet of steam. The most suitable proportion is about 4·7 to 5 cubic feet per square foot of lead.

The question now is, in which way the single chambers are to be combined—in particular, Where must the connecting tubes enter? In any case, at the small ends, so that the gas shall travel right through the length of the chambers. But some prefer to introduce the gas near the bottom, and take it away near the top, others the reverse way; the latter is more usual. If H. A. Smith's theory were correct, the gas ought both to enter and to pass out close to the top, as there must always be a draught towards the bottom; but Schwarzenberg found, in a special case, that the yield of vitriol with the just-described arrangement was only 150 per cent. on the sulphur, whilst after altering the path of the gas, so that it entered near the top and passed out near the bottom, it at once rose to 285. Schwarzenberg points out that the temperature of the gas permits us to infer the time which has elapsed since it left the burners, and consequently its path through the chambers. [The heat generated by the reactions themselves must modify this to a certain extent.] In the first chamber he found immediately below the top, where the gas from the sulphur-burner entered, 53° C.; at the opposite end, where it left for the second chamber, 49° C. 6 feet 6 inches above the bottom the temperature was 47° C. all over the chamber, and 5 feet 3 inches above the bottom, all over, 45½° C. From this he inferred that the gas first spreads all over the chamber near the top, and then sinks down in uniform horizontal strata right across the section of the chamber, fresh gas taking its place. He then divided the chamber, as shown in fig. 125, into two compartments by a perpendicular partition *a b* reaching down to 18 inches above the bottom; and now he found the following temperatures:—near the top of the first chamber, above the inlet for the gas, at *c*, 60° C.; at *b*, 18 inches above the bottom, close to the partition, 52½°; at the same height in the second compartment, at *d*, only 50°, but near the top, close to the partition, at *e*, still 51½°; at the opposite end, at *f*, only 48°; in the horizontal stratum shown by the dotted line *g h*, 5 feet 3 inches above the bottom, at all points distant more than 5 feet from the partition, 46½° was found. From this follows that the gas travels from *c* to *b*, and into the second compartment, in which it rises at once close to the partition; it again spreads along the top and gradually sinks down; so that near the partition two currents, an upward and a downward one, must pass each other, of course not divided by any sharp line, but mixed to a certain extent near their limit, so that at *d*, only 18 inches from the partition, the medium temperature of 50° was found. Schwarzenberg from all this draws the conclusion that the gas ought to be introduced into the chamber near its top and taken away near the bottom; if it is introduced near the bottom, there is a loss of draught both by the loss in height and

Fig. 125.



by the mutual checking of the two currents of gas generated within the chamber. This must influence the process, but need not necessarily disturb it. If, however, the gas be not taken away near the bottom, but near the top, a considerable loss is the consequence; for the gas is drawn away too quickly, the space underneath becoming stagnant and only acting gradually as gas slowly enters it by the law of diffusion. This was strongly illustrated by the above-mentioned raising of the yield from 150 to 285 when the pipe, formerly connecting both chambers just below the top, was so altered as to take away the gas from just above the bottom of the first chamber and introduce it near the top of the second chamber.

It has been found, in the practical experience of many large works, that it is not necessary to arrange the connecting pipes diagonally, as prescribed by Schwarzenberg; they are often found about midway, but best about the height of a man's head, leading straight from one chamber to the next. This does not at all contradict the argumentation of Schwarzenberg.

The total *cubical contents* of a set of chambers must bear a certain proportion to the quantity of acid to be produced, several special circumstances modifying that proportion. Thus it is certain that for pyrites more chamber-space is needed than for sulphur; we have seen above (p. 256) that the relative proportion may be stated as 1 : 1·314. But now the question is, What is the absolute amount of space needed? Properly speaking, the connecting pipes, if they are of great length, and the Glover and Gay-Lussac tower ought also to be included in the calculation, possibly to a larger extent than corresponds to their cubical contents.

The consumption of nitre also influences the chamber-space; within certain limits a larger consumption of nitre may compensate for a smaller space.

Partly from this the widely divergent views on this point may be explained, but not entirely; for on the Tyne some manufacturers obtain about the same yield as their neighbours possessing half as much chamber-space again, although the pyrites, the general construction of the plant, and their consumption of nitre are as nearly as possible the same. In the following we shall reduce all statements to cubic feet of chamber-space required for burning 1 lb. of sulphur daily, taking, in the case of pyrites, the sulphur bought, not that actually burnt.

Schwarzenberg states the proportion for a small set of chambers and for *brimstone*, without a Gay-Lussac tower, to be 32 cubic feet for 1 lb. brimstone, with a consumption of 6 per cent. nitre; as the lower limit he states 29 cubic feet—even less in larger works, of which he gives some actual figures, viz. 22·8, 24·6, 24, down to even 16 cubic feet; but in the latter case much more nitre was used, or acid was lost. Knapp (Chem. Technologie, i. part 2, p. 337) states 17·2 to 23 cubic feet. Fournet, at Bordeaux ('Rapport du Jury international,' 1867, vii. p. 18), states that in chambers of 400 cubic metres capacity he daily burned 500 kilograms of brimstone (=12·8 cubic feet per lb.) with the assistance of several pipes filled with coke, and that his yield was 300 o. v. on 100 brimstone (?).

For *pyrites* Schwarzenberg states that the theoretical proportion for small chambers=42 cubic feet, for large ones=36·8, on each lb. of sulphur actually burnt, or, say, 34·4 per lb. of sulphur bought. Bode states as the figure found in several German works 29·6 cubic feet per lb. of sulphur bought, with a consumption of 4·75 per cent. of nitre (which is now much smaller). From sundry English alkali-works the author can state the following proportions:—

I.	II.	III.	IV.	V.
28	25	20	18	16 cubic feet.

I. and II. are considered too high by the chemists of the respective works themselves; but it should be stated that the same space was employed in 1864, when 30-per-cent. Irish pyrites was used, for which it was more suitable. III. (viz. 20 lb.) is a proportion employed at many large works; but IV. and V. are found in works having as good a yield of acid (270 to 288 o. v.) and no larger consumption of nitre (3½ to 4 per cent.). In all cases rich Spanish or Norwegian ore was burnt, and both Gay-Lussac and Glover towers were used. From this it follows that under the same conditions 20 cubic feet per lb. of sulphur charged is amply sufficient, and 18, or even 16, will do; but the latter certainly is the lowest allowable limit. This agrees with a statement of Wright's (Chem. News, xvi. p. 94), who demands 16 to 19·2 cubic feet.

The usual proportions in the south of France are stated by Favre (Monit. Scient. 1876, p. 271) as follows. Each square metre of grate-surface in the pyrites-burners daily receives 270 kilograms of

40-per-cent. pyrites, and corresponds to 180 cubic metres of chamber-space. This means 1·66 cubic metre for each kilogram of sulphur charged, or 26·5 cubic feet per lb.

In the north of France the author has generally found about 8 cubic feet per lb. of pyrites, or about 17 cubic feet per lb. of sulphur charged, with good yields and low consumption of nitre, but only for low or medium temperatures; in summer $\frac{1}{4}$ to $\frac{1}{3}$ more chamber-space is required.

It should not be overlooked that the best proportion of chamber-space to the sulphur burnt cannot be fixed absolutely, but that several conditions have to be taken into account. First of all, it is not indifferent whether rich or poor pyrites is used. The latter requires proportionally more air and furnishes poorer gas, and thus needs more chamber-space. At Oker each cubic metre of chamber-space yields 2·85 kilograms chamber-acid of 106° Tw. in the case of rich ores, but only 2·0 kilograms with poor ores. The first corresponds to 35·5, the latter to 48 cubic feet of chamber-space for each lb. of sulphur actually recovered in the vitriol. Furthermore it is very important with what temperature the gas enters the chambers. The better it is cooled, the less volume it occupies for equal weight, and the less chamber-space is used. For this reason a Glover tower, which cools the gas very completely, causes a saving in chamber-space. It has also been noticed at many works (compare above) that in winter for the same chamber-space either a good deal more pyrites can be burnt or less nitre is consumed than in summer.

The chamber-space might be extremely restricted if in lieu of air pure oxygen were used in the process. This was patented in 1871 by Terrell, Hogg, and Tomlinson, and again proposed by Bode (Ding. Journ. ccxvi. p. 453), who justly calls it a consideration of the *future,* which in the present does not concern us.

Each set of chambers must contain a number of *auxiliary apparatus,* which in part are absolutely necessary for the process, in part serve to check it chemically and technically: the former are essentially those for introducing the nitre, the steam, and the air; the latter, smaller, apparatus shall be described first.

Drawing-off the acid is never done by cocks attached to the chambers, which might be made of hard lead (4 to 5 Pb to 1 Sb), but that they would readily get stopped up with sulphate of lead, and could not very easily be repaired when leaking. It is best to put beside a chamber a round or square lead box, open at the top, of the same height as the upstand of the chamber-bottom, and connected at or near the bottom by a wide pipe with the chamber; or a suitable piece may be burnt on to the chamber, as shown in fig. 126, and the connexion made by a slit. The box may be provided with a stopcock; but more usually, as shown in the figure, it carries in its bottom a valve-seat *a* of regulus metal, into which fits a conical plug *b* of the same metal provided with an iron handle covered with lead. The running-off pipe *d* is either burnt to the valve-seat or joined to it by an open funnel; the latter permits the running-off to be more easily observed, but is apt to occasion running over, by getting stopped up. Or, as shown in fig. 127, a lead siphon may be employed, to which at the bottom two cups, *a a*, are joined, which always keep it filled, so that it begins to act as soon as one of its limbs has been put into the acid. The second limb then enters into a large funnel of the running-off pipe *b*.

Fig. 126.

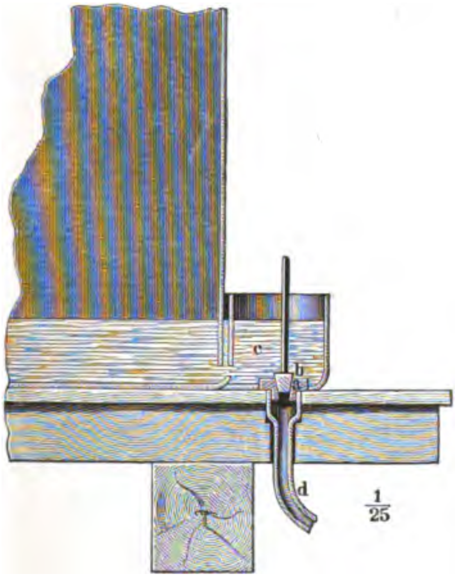
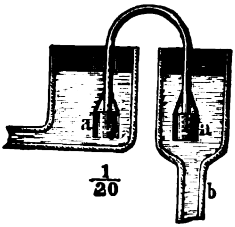


Fig. 127.



The arrangement shown in fig. 128 is a very good one. The siphon *b* is firmly attached to the box *c*, or within the upstand of the chamber. A cylinder *d*, surrounding the outer limb of the siphon, is so suspended that it can be drawn up or down by means of the chain *e* and the pulley *f*, and fixed in any position by the hook *g*. The cylinder *d* forms a continuation of the outer limb of *b*; when it is quite drawn up, so that its overflow *h* is at a higher level than the acid in *c*, it will cease to run; but when *h* gets below this level, the siphon will at once begin to act, and the more quickly the more *d* is lowered. Thus the acid can be run off with more or less speed and with the utmost cleanliness.

Fig. 128.

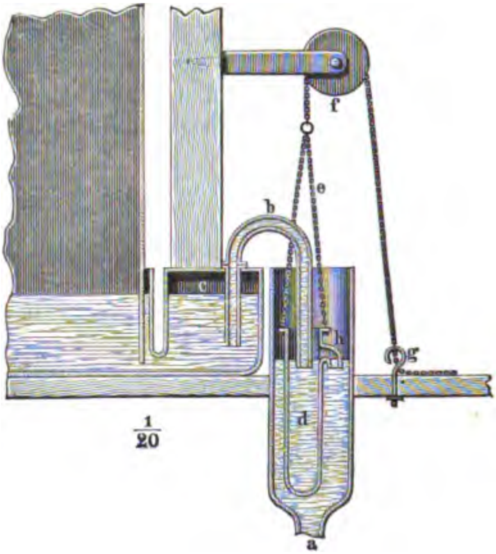


Fig. 129 represents a siphon suitable for hot acids in any part of the works. To the top of the siphon *a a* there is joined by a bent tube a closed lead vessel *b*, which by an elastic tube is connected with the open vessel *c*. The latter is filled with acid and lifted into the dotted position, whereupon *d* and then the siphon *a* are filled; *c* is then lowered, whereupon the siphon begins to act, some acid running back from *b* to *c* and thus producing a partial vacuum.

Another contrivance for filling and putting in siphons, which is especially adapted for acid-carboys, is shown in fig. 130. An ordinary glass or lead siphon is inverted and filled with water or acid; it is then closed by the long, very pointedly conical, flexible india-rubber plugs, *a a*, which are fixed on bent wires. The man holds these wires fast against the limbs of the siphon, whilst he lowers one limb into the vessel to be emptied, and then, by pushing down both wires, loosens the india-rubber plugs, whereupon the siphon begins to run. Thus one man may manipulate the siphon without any assistance.

Fig. 129.

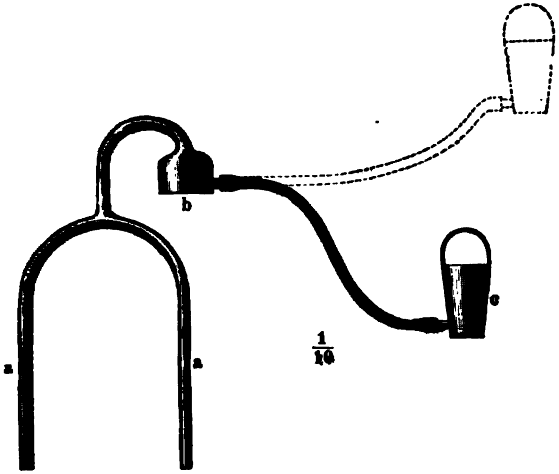
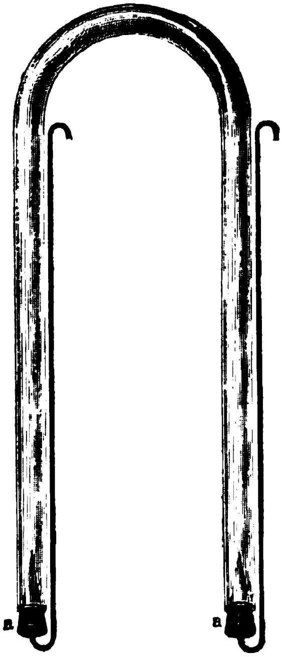
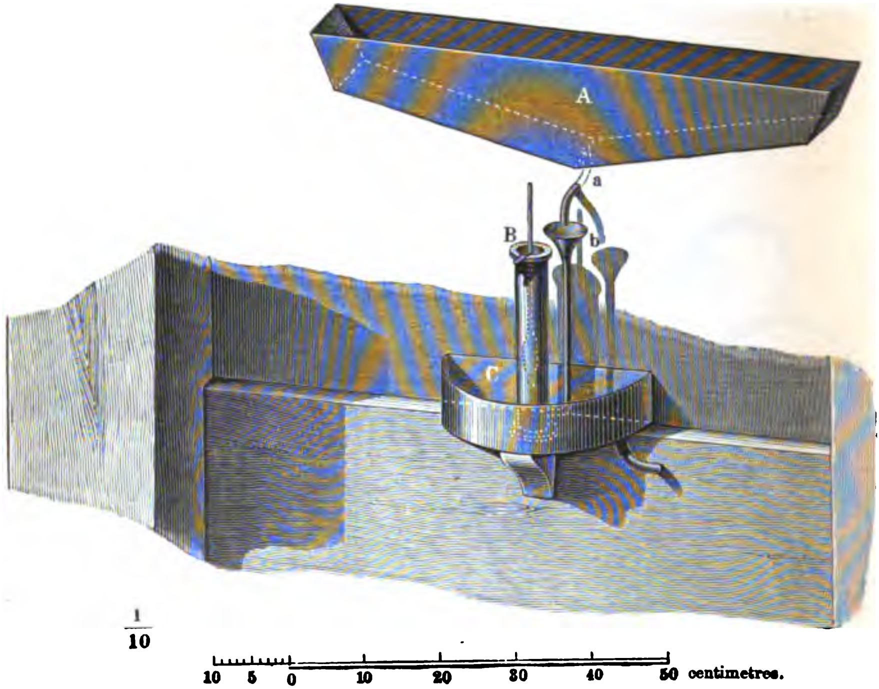


Fig. 130.



Acid-dishes (*drips*) are placed inside the chambers, in order to examine the process by ascertaining the quantity, strength, and nitrosity of the condensing acid. They are made in very different ways—for instance, that shown in fig. 131. A is a lead vessel, burnt against the chamber-side about 3 feet above the bottom. The acid caught here runs by the tube *a* through the chamber-side into the lead cylinder B, containing a hydrometer. B is provided near its bottom with a side-branch, *b*, reaching above its top, and ending in a funnel for receiving the acid, which thus constantly runs in at the bottom and out of the top of B into a vessel C, from which it is carried back by a small pipe into the chamber.

Fig. 131.



Many manufacturers have S-shaped drip-tubes in the connexions between the chambers, for a similar purpose. Many others do not trust to the collectors burnt to the chamber-sides, but place dishes at some distance from the side within the chamber. These rest on feet made of lead tubes, or upon a stand of stoneware, so as to be elevated above the level of the acid; and they have an outlet leading outside the chamber. In some works, for instance at Aussig, both kinds of drips are fixed side by side; and it is noticed that those fixed to the sides always yield acid of 6° to 10° Twaddle less than the inner drips, evidently because on the sides more aqueous vapour is condensed along with the sulphuric acid. This certainly is "condensation" in the proper sense—not condensation of acid, but of water, or just the contrary of the thing intended by several "inventors."

For taking samples of the bottom-acid itself there is usually a recess made in some part of the chamber by dressing back the lower part of the side. Some, in order to be quite sure, always take the sample out of the chamber itself through a special small man-hole luted with moist clay; in this case there is a small loss of gas, but no danger of getting stagnant acid. Such a man-hole is shown in fig. 132ª in section. The large *man-holes* may be made in exactly the same way; or else their lids may fit into a groove luted with damp clay, as shown in fig. 132ᵇ. Large chambers are fitted with several acid-drips, man-holes, &c.

Fig. 132ª.

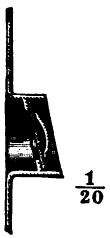
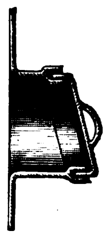


Fig. 132ᵇ.

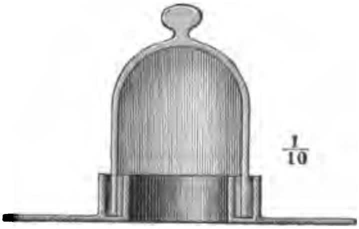


For taking the samples themselves a dipper of lead or glass is employed, which is lowered slowly, so as to get all layers of the acid into it. There is often a great difference between the top- and bottom-acid.

In German works there are regularly *thermometers* fixed about every 30 to 50 feet of the length of a chamber, whose mercury-vessel is inside, and whose scale is outside the chamber. This means of observing the temperature is undoubtedly infinitely better than the rough one commonly used in England, by touch of hand.

Sometimes also *clay plugs* are put into holes made in the chamber-sides, in order to indicate the pressure inside the chamber; this is better done by simple glass pressure-gauges. The tension of the gas is also seen by lifting the lids of the small man-holes (fig. 133) which are always made on the top of the chambers, with hydraulic lutes, and which generally consist of glass jars, so as to give light for observation through the side-windows (see below).

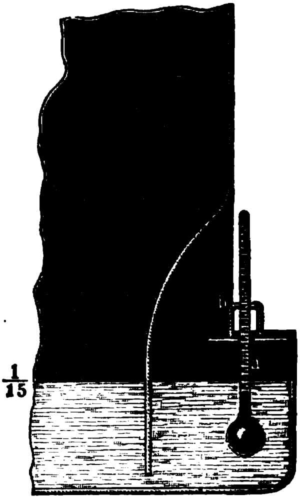
Fig. 133.



A very sensitive *pressure-gauge* has been described by Vogt (Journ. f. prakt. Chem. xiv. p. 284). The pressure is observed by the movement of a small air-bubble playing in a horizontal glass tube of 4 or 5 millimetres diameter. The glass tube, apart from this bubble, is filled with water or another liquid, and is connected on each side with a bottle tubulated near the bottom. One of these bottles is 15 to 16 centims., the other 6 to 8 centims. wide; the liquid stands at the same level in both. The pressure within the lead chamber is made to act upon the surface of the liquid in one of the bottles, and its amount measured by the place of the air-bubble. The apparatus is all the more sensitive the greater the difference between the diameter of the tube and those of the bottles. There is a contrivance for admitting a bubble of air previously to using the apparatus, and for again equalizing the levels after use.

For *gauging the height of the acid* there are either stationary lead gauges (which, however, are difficult to read-off exactly), or accurately divided copper rods, which are dipped in every time, but always in the same place, since the chambers are never absolutely level, or glass floats like that shown in fig. 134, *a*, the stem of which slides in a small lead frame, *b*, whose upper edge serves as an index for reading-off. The float will sink more or less in the acid, according to any alterations in its specific gravity. To make this cause of inaccuracy less sensible, the ball of the float is made pretty large. The floats are the most convenient for reading-off.

Fig. 134.



A very important assistance in judging of the chamber-process is afforded by *glass windows* or *sights*, which permit the colour inside the chambers to be observed. Whoever has once got used to them will never do without them again. These windows are 8 or 9 inches square, and are placed, at a convenient height for looking, in those places in the chamber-side which lie in a line with the glass man-hole lids in the chamber-tops; thus they are sufficiently lighted. Where the chambers are roofed in, light must be procured in some other way (for instance, by two opposite windows corresponding with a window in the chamber-shed, &c.). The chamber-glasses are put into small lead rebates, and luted with white lead and boiled oil. Sometimes the assertion is made that the colour of the gaseous mixture, looked at across the width of the chamber, or in the diagonal line from the side to the man-hole lid in the top, is too deep, and that "sights" in the connecting-tubes are preferable; but just the opposite is the case, since the observations are evidently far more accurate, and any alterations of colour much more easily perceived, in the former than in the latter case. Only in the first part is the gaseous mixture, through copious condensation of acid, too opaque for observing its colour; but just there it is quite unnecessary, for only in the back parts of the set is it important to have always an excess of red vapours.

Apparatus for introducing Nitric Acid into the Chambers.

These are divided into two classes, according to whether nitric acid enters the chambers in a *gaseous* form, mixed with the burner-gas, whose heat evolves it from a mixture of sodium nitrate and sulphuric acid, or whether it is made in a *liquid* form in special apparatus, and introduced as such into the chambers. Opinions still differ on the point, which of the two plans is best. The plan of introducing gaseous acid, which formerly was quite general, and is still so in England, but only partially used on the Continent, has the advantage of greater simplicity and of saving labour and fuel. The advantage sometimes claimed for it of smaller loss than by making in the first instance liquid nitric acid, is not very great; for some nitric acid is easily condensed during the conveyance of the gas to the chambers, and may corrode brickwork, iron, &c., whilst liquid nitric acid is always introduced exactly in the place where it is needed. The presence of nitric acid in the burner-gas will also induce a premature formation of sulphuric acid in the same, especially if it be much cooled; but the Glover tower obviates any inconvenience arising from this. On the other hand, some are afraid that the nitre-ovens may get so hot that a portion of the nitric acid will be decomposed down to NO or even to N; but mostly the men employ so much sulphuric acid for decomposing the nitre, that this cannot easily happen, nor are NO and N formed so very readily as was formerly apprehended (see below).

The advantages of introducing nitric acid in the *liquid* form are the following :—avoiding the entrance of false air into the chambers and the escape of burner-gas into the atmosphere, both of which occur in many (not all) systems of employment of gaseous acid; the possibility of employing as much nitric acid and as quickly as desired, whilst in the other case this depends on the heat of the burner-gas, which during a bad process, just when most nitric acid is needed, proves insufficient; lastly, and most of all, the exact regulation possible with liquid nitric acid, and its continuous supply, whilst gaseous acid is always given off from the nitre-mixture very unequally. These advantages have induced many continental manufacturers to adopt liquid nitric acid. But it is not true that a saving of nitre can be effected in this way; Muspratt ('Dictionary of Chemistry,' ii. p. 1029) reports that, on the contrary, a continental manufacturer, who previously worked with liquid nitric acid, after having seen the use of solid nitre in England, had saved one third of his nitre by introducing the English plan. This simply proves that that manufacturer had not been very careful before, and is no rule of action whatever. The opposite transition has been much more frequent. Liquid nitric acid, however, will do harm if the apparatus for introducing it is not constructed in such a way as to completely volatilize it or convert it into gaseous products before it reaches the chamber-bottom, since it will act upon this. Accordingly, sulphurous and aqueous vapour, which decompose the nitric acid, must be brought into as complete contact with it as possible.

In very large works the employment of solid nitre has this advantage, that the chambers are not exposed to the damage possible with incautious handling of nitric acid, whilst, on the other hand, the irregular evolution of gas from the nitre-mixture is equalized by employing several decomposing apparatus, and charging them by turns, say, once every hour, just after a fresh pyrites-burner has been charged; thus the stronger evolution of nitre-gas runs parallel with that of sulphurous acid. Still better is a contrivance for supplying gradually, and not all at once, the sulphuric acid serving for decomposing the nitre. In fact the best English works, all of which employ solid nitre, work with as small a consumption of it and as good a yield of vitriol as the best of the continental works employing liquid nitric acid; and on the Continent as well, many manufacturers work quite as well with solid nitre as their neighbours with nitric acid.

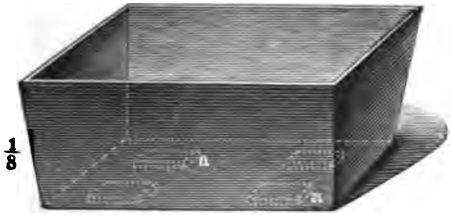
After very careful investigations, the author would sum up his own opinion as follows:—With careful work, and when dividing the nitre among several apparatus charged in turn, there is *no* more consumption of nitre when it is employed in the solid state. Liquid nitric acid has the advantage of easy regulation and of avoiding any loss of gas; but the latter is equally attained by *good* apparatus for solid nitre. The advantages of nitric acid are *more* than outweighed by the undeniable extra cost and trouble of making it, and by the danger to the men in handling the carboys. The author in no case would think of employing nitric acid, except when this acid is made at the works for sale; but there are even works where this is done and yet the acid-chambers are worked with solid nitre. Unfortunately, attempts to feed with solution of nitrate, which would combine every advantage, have not been very successful, as we shall see below.

We shall now describe both ways of introducing nitric acid, and begin with the

Introduction of Solid Nitre.

The apparatus serving for this has been partially described in a former chapter, along with the sulphur- and pyrites-burners. The drawbacks have been pointed out which attend placing the nitre-pots within the burners, or, generally, in such a way that the acid sulphate boiling over can run into the burners. Accordingly, recently there has always been a special *nitre-oven* constructed by enlarging a suitable place in the gas-flue. It is situated either above or, preferably, just behind the burners, and provided with the necessary working-doors and a cast-iron saucer for collecting what boils over. The nitre-pots themselves have various shapes—for instance, that shown in fig. 135; at *a a* ledges are cast on the bottom, which facilitate pushing the pots backwards and forwards. They hold from 8 to 12 lb. of nitre.

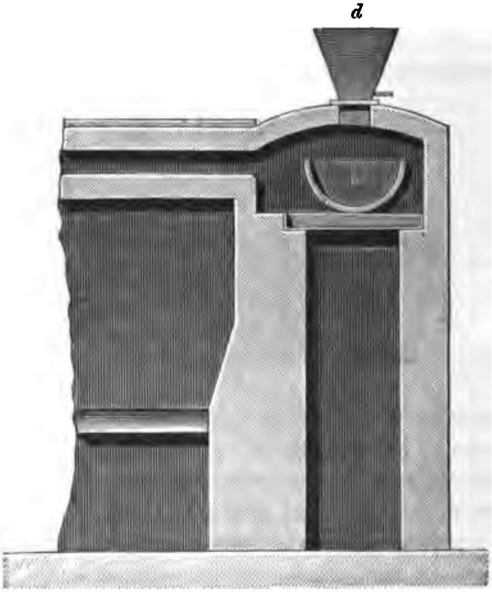
Fig. 135.



The "potting" with these pots, which, strange to say, are met with in some works otherwise abreast of the times, is very troublesome and imperfect. During the emptying and refilling of the pots the doors of the nitre-oven are wide open, which does even more harm than in the case of the burners. The heavy pots, along with their melted contents, have to be taken up with long fork-shaped tools and emptied, which requires great strength and skill. The pots, freshly charged with nitre, are placed just within the door of the oven; the necessary acid is poured in from a jug by superficial estimation, and the pot pushed into its place; not till then can the door be closed. If the draught is good, a great deal of air must enter, meeting not even the same resistance as in the burners; if it is not very strong, which will more usually be the case, so much gas escapes that it can be smelled for some distance. Special dampers would partly obviate this, but are rarely met with. (Such dampers are mentioned in the official Belgian Report of 1855, p. 23.) The pots are quickly worn out, and must be replaced, especially if chamber-acid is employed in them. They last much longer if acid of 140° Tw. is used in them.

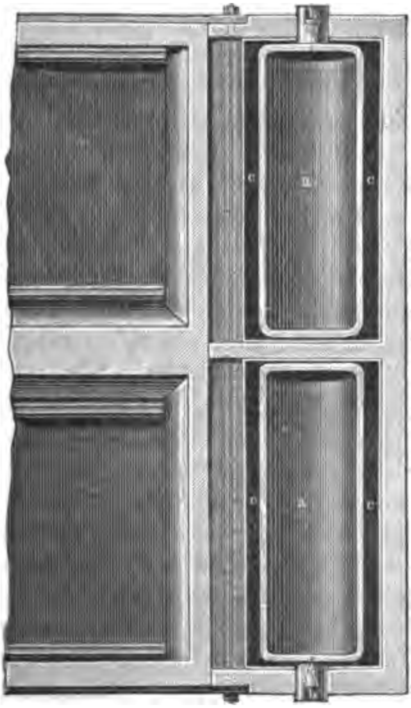
A much more perfect plan is that of decomposing the nitre in a *fixed apparatus*, and running off the acid sulphate (nitre-cake) in a liquid form. This consists of a semicylinder of cast iron, *a* (figs. 136 & 137), with a cast-on tube *b*, bored somewhat conically.

Fig. 136.



The latter projects out of the nitre-oven, and during the working is closed by a ground-in iron plug with a long handle. Outside there is a cast-iron saucer for holding the nitre-cake, which at once solidifies. The internal saucer, *c*, catches the boilings-over. The nitre is introduced by the hopper, *d*, which is provided with a damper; and after putting in the damper again, it is made gas-tight by filling up with the next charge of nitre. An S-shaped tube (not shown in the diagram) serves for running in the vitriol, for which it is best to provide a small tank with a siphon or stopcock. The vitriol ought to be run out of this tank by a pipe with a very fine point into the S-shaped pipe, so that the running shall take a long time, and the nitre be only gradually decomposed. Sometimes an iron scraper with a long handle (passing through one of the ends of the oven) serves for stirring up the mixture in the pan. The hole for this must be kept air-tight with clay. An apparatus of the size drawn here holds 56 lb. of nitre, which can be easily decomposed in two hours. In any case there should be two or more of these apparatus, so as to make the current of nitre-gas more regular by charging them in turns.

Fig. 137.



Scale $\frac{1}{36}$.

Even preferable to the arrangement here drawn is that of placing the nitre-trough on iron rails, so that the burner-gas can play round the bottom as well. The saucer for the boiling-over stuff, which forms the bottom of the nitre-oven, must then be placed somewhat lower.

Introduction of Liquid Nitric Acid.

The nitric acid is employed of such strength as is obtained without difficulty from the above-described retorts. Acid of 38° B. (=72° Tw.) just contains 50 per cent. of NHO_3; and 100 parts of it correspond to 67·46 of pure, or 71·01 parts of 95-per-cent. nitrate of soda.

It is of the greatest importance for the process to supply the acid in an even, continuous way, and to regulate the supply to a nicety. This can be done most simply by a Mariotte's vessel, as shown in fig. 138 on a scale of 1 : 10. The stoneware vessel, A, containing the nitric acid, is closed by a caoutchouc cork, *a*, holding a glass tube, *b*. The latter is the only channel for the air which must take the place of any acid running out through the cock, *c*. As the liquid above the level *h h'*, down to which the tube *b* reaches, is supported by atmospheric pressure, only the height of acid below this can influence the speed of outflow; and this remains constant till the level of the acid has sunk below this point. The glass water-gauge, *d*, and the lead scale, *e*, admit of observing the height of liquid within the vessel. The latter is filled up through the tube *b*, which ends in a funnel at the top. During this either the cork must be raised, or it must be provided with a separate open glass tube which at other times is kept closed. The funnel *f* carries the acid into the glass or stoneware pipes conveying it into the chambers.

At some works there are two tanks, E E, fig. 139, which are filled up in turns, one of them every 12 hours, or both of them every 24 hours. The acid is running continually out of both. When one of them is half empty, the other one is just full; and thus the variation of pressure is compensated to a certain extent; but this plan cannot at all vie in regularity with a Mariotte's bottle.

The nitric acid must be spread over a large surface within the chamber, so as to expose it sufficiently to the action of sulphurous acid. This is done by "cascades" of stoneware, such as are shown in fig. 139 on a scale of 1 : 50. At A the vertical section through the centre of a set is seen; B shows the lower part in section, the

Fig. 138.

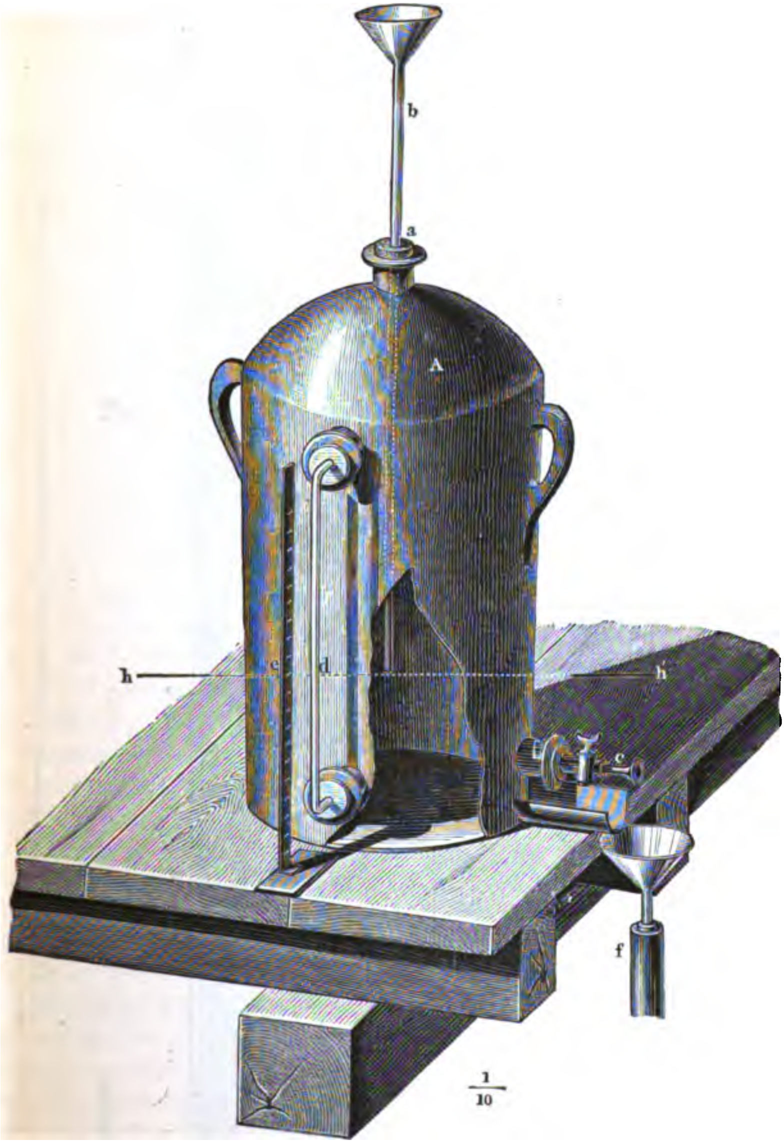
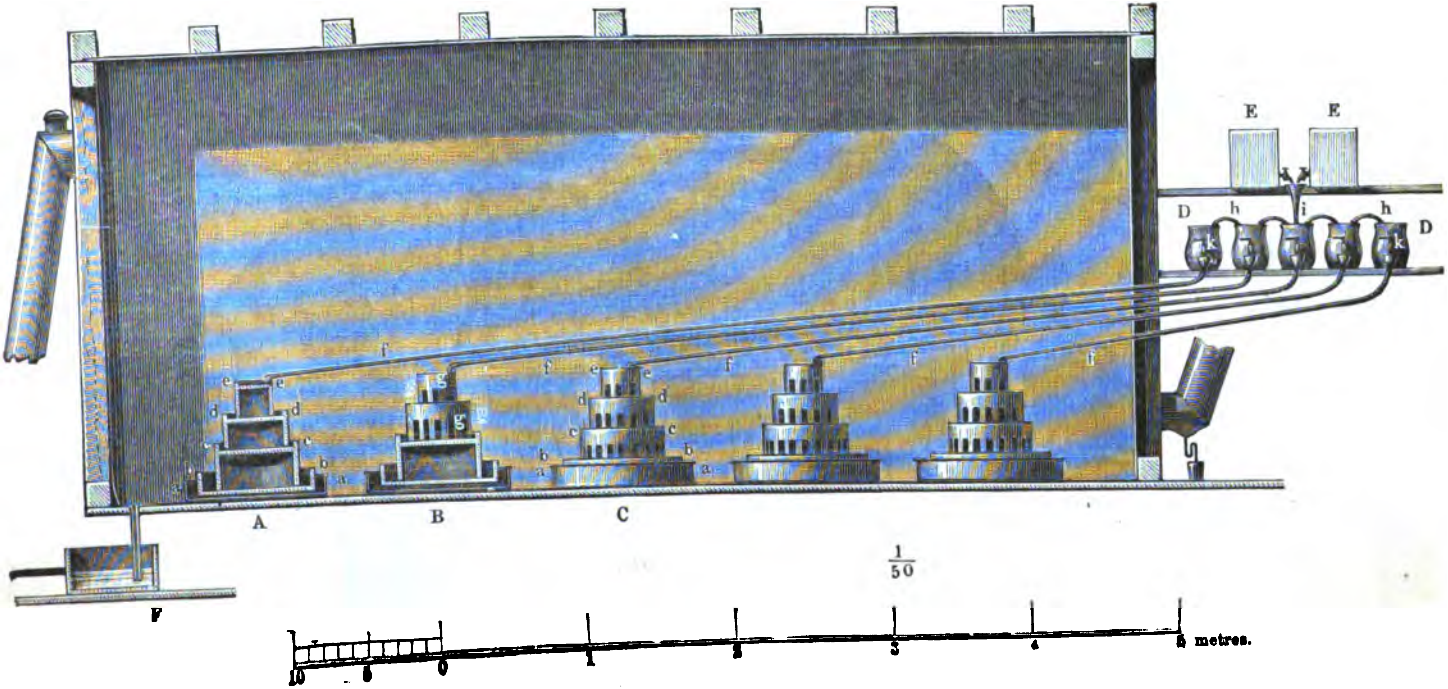


Fig 139.



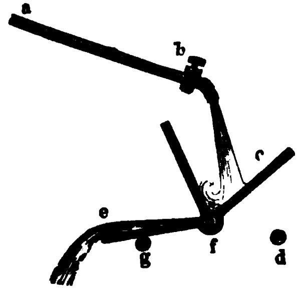
upper part in elevation; C gives an outside elevation of the whole. Each set consists of four stoneware cylinders placed one within another. The lowest, *b*, is 2 feet 7½ inches wide, and stands in the lead dish *a* on brimstone powder, to make it steady. Each of the upper vessels is 8 inches narrower than the next lower one, so that the whole forms a cascade for the nitric acid supplied at the top. The lowest vessel, *b*, is dish-shaped. Each of the upper ones is divided into two compartments by a bottom about 1 inch below the upper edge; thus the nitric acid must always run over these edges to get into the vessels below.

The lower compartments all have round holes, *g*, through which the gases as well as the nitric acid can get inside as well, and thus act on a larger surface.

The nitric acid is supplied through the stoneware pipes *f*, passing through the side of the chamber, from the jars D. These are fed through *i* from the tanks E E or from a Mariotte's bottle; they communicate by wide siphons, *h*, and are thus always at the same level. Each jar supplies one of the cascades, the cock *k* regulating the feed; these cocks are fixed at such a height that the siphons can never run dry. This is much better than the method figured in Payen's 'Précis,' in which only one of the cascades is fed directly, and the other cascades only by branch tubes from the first, since this can never be done in such a way that all the cascades receive the same quantity of nitric acid: one of them (the first) will get most of it; and a portion of it will probably arrive at the bottom undecomposed and damage the lead.

Sometimes the acid is spread by an oscillating trough made of stoneware, as shown in fig. 140. The tube *a* and cock *b* convey the acid from a reservoir into the compartment *c*, at present the top one. When this is full, the trough turns round its axis *f*, its centre of gravity being changed, till it is stopped by the rod *d*, and hereby empties itself. Thus the second compartment, *e*, is raised up; it arrives below the opening of *b*, and is filled in its turn; then it tilts over to the other side, where it is stopped by *g*, and the play

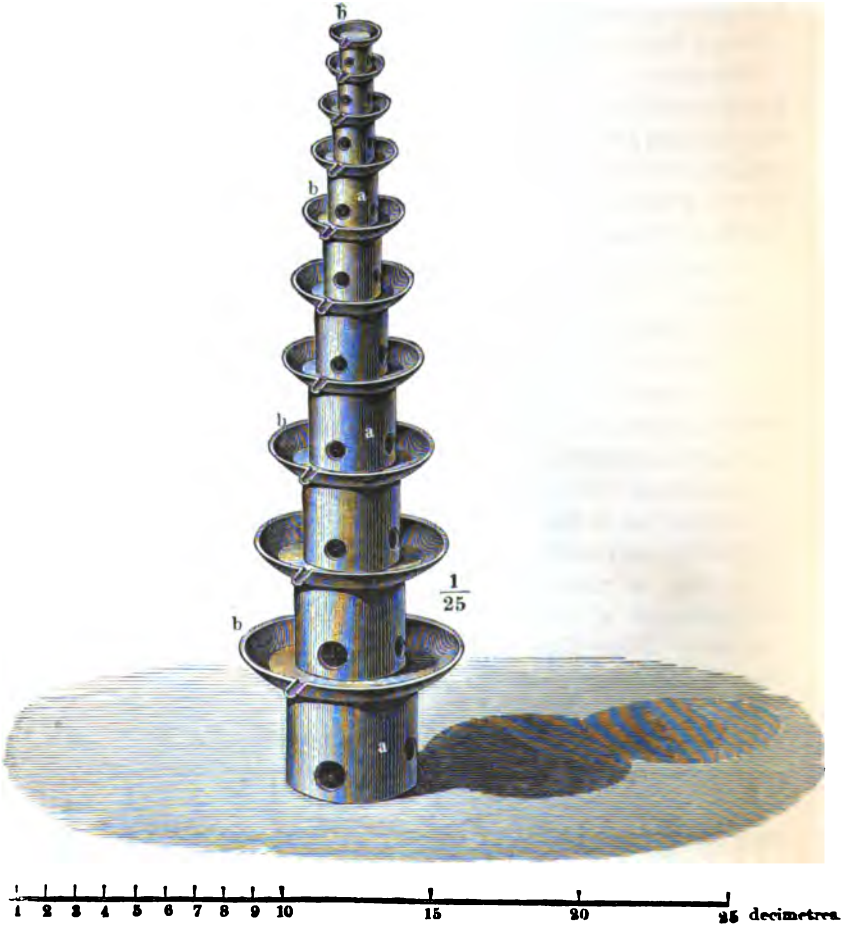
Fig. 140.



begins again. The acid intermittently poured out is caught in a vessel conducting it to the individual cascades in such narrow tubes that each tilting of the troughs fills them all at the same time. This saves the jars and cocks shown in fig. 139; but some of the narrow tubes are easily stopped up without this being noticed; and the oscillating trough itself is very liable to get fixed from one cause or another.

In lieu of the small cascades, at many works a simpler apparatus has recently come into use, where the whole supply of nitric acid enters at a single place. Such is the apparatus shown in fig. 141,

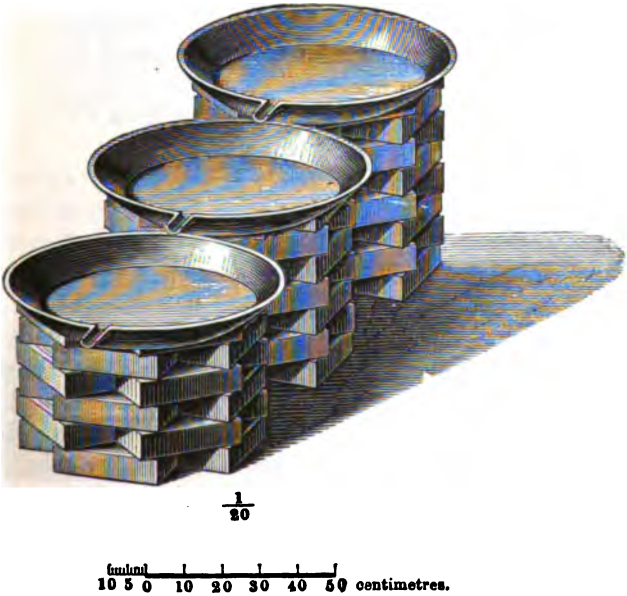
Fig. 141.



on a scale of 1 : 25. It is a column composed of cylinders, *a*, and shallow saucers, *b*, all made of stoneware, diminishing in size from the bottom upwards to the top, so that the nitric acid runs over from one into another. The lowest saucer is 2 feet 6 inches wide and 2½ inches deep, the uppermost 6 inches wide and 1¾ inch deep; the cylinders have openings for the circulation of the acid and the gas. This apparatus has the following faults:—When the glass or stoneware tube conveying the nitric acid has to be replaced by a new one, it is difficult to just hit the top dish of the cascade; there is even a danger of upsetting the whole column, owing to its slight stability; and the upper dishes are so small that they are soon filled with mud and flue-dust.

Consequently, most works now employ stoneware dishes of equal size, about 3 feet wide and 2½ inches deep. Twelve of these are placed terrace-wise, one behind the other, in one of the chambers, so that the spout of each projects over the next lower dish, and empties the overflow into the latter. The dishes are placed on loosely-put-together firebricks, as shown in fig. 142 on a scale of 1 : 20.

Fig. 142.



Whilst the nitric acid slowly runs through the above apparatus, it is reduced by the sulphurous acid surrounding it to hyponitric and nitrous acids, which get mixed with the other gases; the sulphuric acid formed in this process, if the spreading is properly done, arrives at the bottom free from nitric acid.

Formerly the nitric acid used to be decomposed in two "tambours" (that is, small lead chambers) about 22 × 10 × 12 feet, or cylinders of 10 to 13 feet diameter and 12 feet height, placed between the burners and the main chamber. The second of these contained the above-described spreading-apparatus; it stood at a higher level than the first tambour, into which it emptied its acid, and which only served for further exposing it to sulphurous acid, and completely driving off the nitrogen oxides. This first chamber received enough steam to prevent the formation of chamber-crystals, or to decompose them if they arrived in solution from the second chamber; the acid collecting in the first small chamber ran away into the main chamber. The first tambour is unnecessary; with proper regulation the nitric acid can be completely decomposed in the first apparatus by means of SO_2 and steam; but the latter ought to be supplied to such an extent that the sulphuric acid formed contains rather more than four molecules of water to each molecule of acid. At some French works the above-described faulty arrangement of the cascades caused the acid in the second tambour to contain a good deal of nitric acid.

Recently at many works the tambours have been abolished, and the process carried on in the main chamber.

The descriptions of cascades hitherto given, mainly according to Schwarzenberg, should be supplemented by some of the most recent improvements. To these belongs Bode's construction (Dingl. Journ. ccxxiii. p. 400), shown in figs. 143–145. The dishes have an upper diameter of 2 feet 3 inches, and 3 inches height. The spout is cut in so low that the acid hardly stands 1½ inch deep. They are supported by stoneware cylinders of three different diameters and varying heights. The nitric acid passes into the chamber through a glass tube, forming an hydraulic joint and fitting into a lead tube soldered into the chamber-side. From the bottom dish the acid runs into a pot, *d*, of thick lead, joined by a pipe to another pot, *e*, outside the chamber. Thus samples can be taken and the degree of decomposition ascertained. To allow the air-bubbles to escape, the connecting-pipe of the pots is bent

Fig. 143.

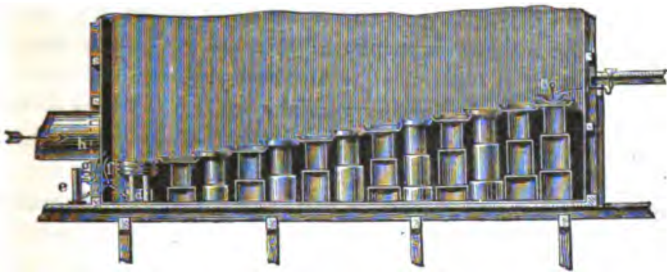


Fig. 144.

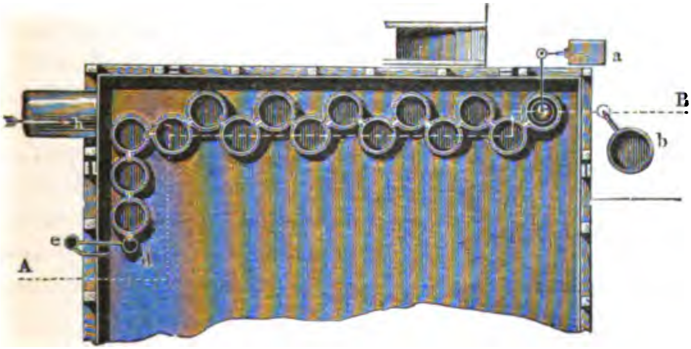
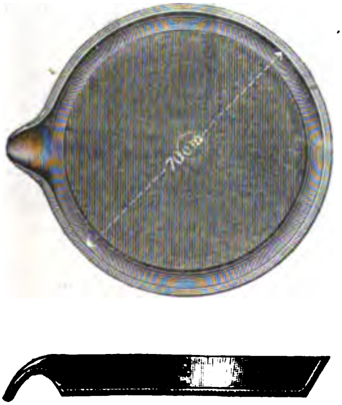


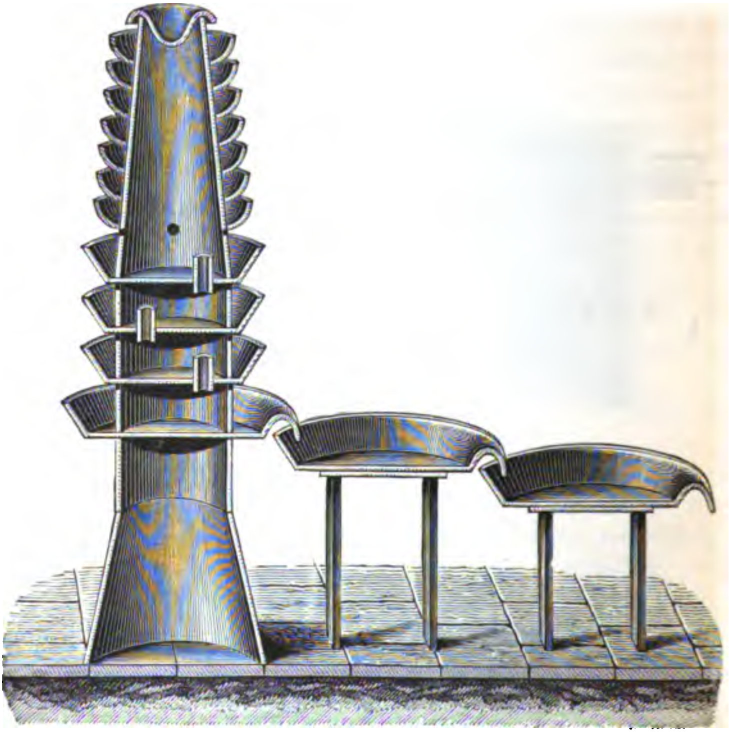
Fig. 145.



upwards and furnished with an air-tube, *f*. From *e* the acid goes back into the chamber by another tube, forming an hydraulic joint and carrying an air-tube, *g*. The burner-gas enters the chamber through *h*; the cascade is so placed that the gas comes into complete contact with it, first of all with the last dishes. Such a cascade suffices for a lead chamber turning out 5 to 7½ tons of vitriol of 144° Tw. in twenty-four hours. Fig. 145 shows the dishes on a larger scale.

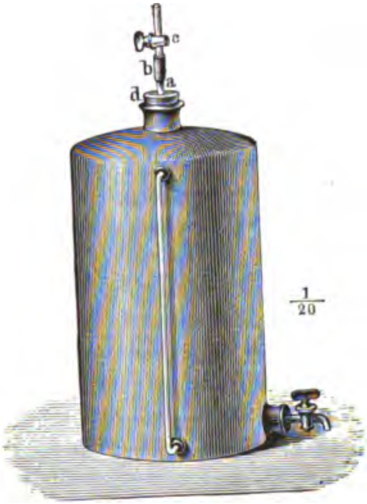
A very good shape of cascade is, lastly, that made by Fikentscher, of Zwickau, and figured in fig. 146; this is recommendable from its large surface and the frequent movement imparted to the acid.

Fig. 146.



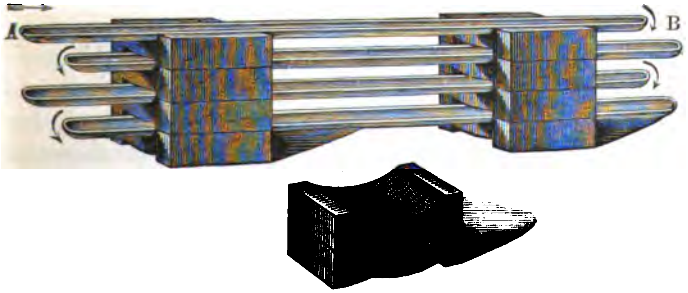
Bode (Dingl. Journ. ccxx. p. 538) has also improved the ordinary Mariotte's bottle, which easily gets stopped up by grains of sand &c. getting into the slightly-opened stopcock. Bode avoids this by opening the cock full bore, stopping the neck of the bottle tightly by a caoutchouc cork (as shown in fig. 147), through which a tube, *a*, goes down to the desired depth, the latter being connected by the elastic tube *b* with a metal or glass cock, *c*, of $\frac{1}{8}$ inch bore. Further improvements in this apparatus have been made by Liebig (Post's Zeitschr. f. d. chem. Grossgew. 1878, part 2).

Fig. 147.



In lieu of stoneware dishes, in France glass spouts of 3 ft. length and $\frac{3}{4}$ in. width are often employed; these afford more surface and are much lighter than the dishes. As seen from fig. 148, they are of unequal height, so that the liquid runs from A to B, runs over in B to a second spout, in order to flow in a backward direction, and so forth.

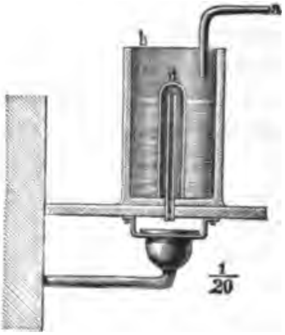
Fig. 148.



According to the size of the chamber and the quantity of nitric acid, from twenty to eighty spouts are placed on pieces of glazed stoneware, shown in the diagram.

In order to be quite sure that the liquid arriving is entirely deprived of its nitric acid, some manufacturers allow the last spout to project outside, so that samples can be taken at any moment.

Fig. 149.



Some manufacturers prefer to run the acid not continuously in a very small jet, but intermittently in larger quantities. For this, nearly always, a siphon arrangement is employed (fig. 149). *a* conveys nitric acid into the stoneware vessel *b*; through its bottom passes a tube reaching about three fourths up its height, and open at both ends. This is covered by the wider tube *d*, which is closed at the top and open at the bottom, so that the acid fills up the space between the inner tube and *d*. As soon as it has got to the top of the former, this, along with *d*, forms a siphon which almost directly empties the contents of *d*, whereupon this is slowly filled till the acid has again risen to the top of the inner tube, and so forth.

By far the simplest method of feeding, which dispenses with all cascades, tambours, &c., is that of running the nitric acid along with the nitrous vitriol through the Glover tower. Up to the very latest time few ventured to do this, because a loss of nitre was apprehended with this plan; but at some of the best-managed works it has now been done for years without involving any extra consumption of nitre.

There is yet a third way of introducing the nitre. Many years ago several works ran their nitre as a *solution in water* into the chambers. This has been given up long since, both because sodium sulphate gets into the acid, which is not allowable for many purposes, and because the lead always wears away very quickly at the point where the solution enters. The same method has been recently patented by Burnard (14th Aug., 1875). The solution of nitre was to be injected into the chamber in a thin jet, or, best of all, at once mixed with sulphuric acid by means of a steam-jet, quite similar to Sprengel's water-spray (compare this). The principal advantage sought for in this process was an imaginary saving of nitric acid, which in the decomposition of nitre by the burner-gas was supposed to be reduced to N_2O

and N. We shall see later on that no sensible decomposition of this kind takes place at all; and any advantage accruing therefrom is far more than counterbalanced by the difficulty of keeping the nitre solution long enough in suspension to completely decompose it and to prevent liquid nitric acid from getting at the chamber-bottom. The process also takes so much steam that the acid in the first chamber gets too weak. This, to be sure, is contradicted by the patentees (Chem. News, xxxvii. p. 203); but no independent favourable testimony has yet been published, and a saving of nitre seems out of the question. It would, however, seem feasible to run a solution of nitre through the Glover tower along with chamber-acid and nitrous vitriol, so that the nitre would be decomposed in the tower itself, sodium sulphate and nitrous acid being formed. Of course, this plan, as well as that mentioned before, is entirely restricted to the case of all the sulphuric acid being intended for decomposing the salt. The last plan is undoubtedly the simplest imaginable one for introducing the nitre, uniting the advantages of both solid nitre and nitric acid—easy regulation, introduction of any quantity at a time, dispensing with all apparatus for introducing the nitre or manufacturing nitric acid, saving of labour and coals (in the case of nitric acid), avoiding the handling of nitric-acid carboys or of fluxed nitre cake, the latter forming an article difficult to utilize to advantage.

Unfortunately, all these advantages are counterbalanced by a great drawback, which has compelled most manufacturers who have tried this process to give it up again: it is found that sodium sulphate crystallizes in the towers, tanks, and connecting-pipes, and causes obstructions. It would be necessary to have two Glover towers for each set, and to run the nitre solution down only one of these, whose acid would not be used for the Gay-Lussac tower, but for the decomposing-pans only. This would be very inconvenient, and for smaller works not at all feasible.

Several other proposals partly carried out in practice have had no lasting success. Thus, for instance, the attempt has been made in France to obtain *oxalic acid* as a by-product in evolving the nitre-gas by heating molasses with nitric acid and conducting the vapours into the chambers. The yield of oxalic acid, however, was not large enough to compete with its manufacture from sawdust by fusing caustic. Not more successful was a proposal of Laing and Cossins, to heat sodium nitrate with arsenious acid or chromium oxide, in order to obtain arseniates or chromates along with nitrous acid for the chamber process (Wagner's Jahresb. 1862, p. 207). On the other hand, it is certainly advisable to convey any nitrous gas generated in making arsenic, antimonic, phthalic acid, &c. by means of nitric acid, which formerly used to be lost, into the lead chambers; but this proposal has very little prospect of being followed out, since the respective works now regularly regenerate nearly the whole of the nitric acid by mere contact of the vapours with an excess of air and water.

A peculiar process has been invented by Dunlop, and is still carried out at St. Rollox, but seems to be confined to that place, being not in use even at the new works at Hebburn belonging to the same firm. A mixture of common salt, nitrate of soda, and sulphuric acid is heated in large iron cylinders; the principal reaction setting in is as follows:—

$$3SO_4H_2 + 2NaNO_3 + 4NaCl = 3Na_2SO_4 + N_2O_3 + 4Cl + 3H_2O;$$

but the further deoxidation of nitric acid will only be prevented by keeping within certain limits of temperature. Thus there remains a soluble residue of sodium sulphate, whilst chlorine and nitrous acid are given off in a gaseous form. The two gases are separated by passing them through a series of leaden Woulfe's bottles filled with sulphuric acid of 1·75 spec. grav.—which retains the nitre-gas, being converted into "nitrous vitriol" and used as such (see below); the chlorine passes through without absorption, and is utilized for bleaching-powder. The advantage of this process is, that chlorine is obtained direct from salt without making any muriatic acid and without wasting manganese. The drawbacks are:—that the nitre-gas has to be evolved again from the nitrous vitriol, which formerly could only be done by diluting with hot water, necessitating a reconcentration of the vitriol; that there is a danger of losing nitrogen compounds; and that the apparatus is somewhat complicated.

The Steam

is always generated in an ordinary steam-boiler since boilers placed above the burners have been given up everywhere. The boilers are constructed in the usual manner, but are mostly made for low pressure, rarely working above two atmospheres, more frequently only at one or one and a half atmosphere; in the south of France they work at three or three and a half atmospheres. A high pressure has no object so long as the liquid is spread over the whole chamber-space; for even low pressure fulfils this requirement and sufficiently assists the draught. Low-pressure steam is more easily kept at the same tension than high-pressure; without this no regulation of the supply of steam to the chambers by the attendant is of any avail. To be sure, high-pressure condenses less readily than low-pressure steam; but this is a doubtful advantage, so long as the steam possesses enough "carrying-power" to convey the minute globules of water right to the other end of the chamber. Experience has shown that this is the case even with low-pressure steam; at most English works they only employ a single jet at one end of each chamber, and find this quite sufficient to supply the whole chamber with moisture.

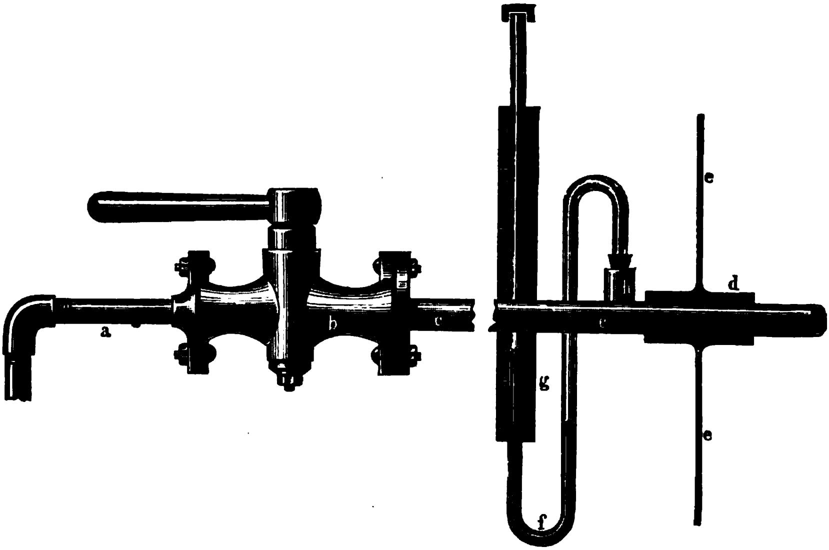
At some large works, in order to control the regularity of tension of the steam, so important for a regular chamber process, *registering steam-gauges* are employed, which show the tension during the whole day on a sheet of paper wrapped round a drum making one revolution in twenty-four hours. Such a gauge, made by Schaeffer and Budenberg, of Magdeburg, is described in 'Dingler's Journal,' ccxxvii. p. 519.

The *conveyance of the steam* to the chambers usually takes place in cast-iron pipes, with one or more branches for each chamber. The main pipes in any case, and, if possible, also the branch-pipes, looking at their great length, ought to be surrounded by bad conductors of heat to restrict radiation as much as possible, and avoid a considerable loss by condensation of water.

The pipes must always be laid with a slight fall towards the boiler, so that the condensed water may run back. Where, from local circumstances, this cannot be done, automatic apparatus for removing the water should be fixed at the lowest points.

Of course the size of the main pipes must correspond to the number and size of the chambers. When more than one steam-boiler is required, they are placed together, and their main pipes connected so as to equalize the pressure. The *branches* for each chamber need not be above 1 inch wide, even for large chambers (up to 70,000 cubic feet) supplied by one jet. They are made of wrought-iron tubes, *a* (fig. 150), sometimes of copper, up to a short distance from the chamber, where they end in a cock or valve, *b*, to which a lead pipe, *c*, equal in width to *a*, is attached and projects into the chamber itself. It is not, however, burnt to the chamber-side *e* itself; but a short wider tube, *d*, is burnt to this, and *c* is loosely put into it, the joint being made tight with tar, cement, &c. In this case, if the outlet is stopped up by lead sulphate, the pipe *c* can be easily drawn out and cleaned, and no platinum nozzles are required (as proposed by Scheurer-Kestner).

Fig. 150.



The same figure shows another commendable contrivance, viz. a simple mercurial *pressure-gauge*, consisting of a bent glass tube, *f*, with a scale, *g*, put by means of a caoutchouc bung into a branch, *h*, of the lead pipe *c*. Thus the pressure *behind* the regulating cock can be observed at any time; and the chamber-manager has thus a means of very exactly regulating the supply of steam. Any water condensed in the gauge can be easily allowed for.

A good steam-*cock* is preferable to a wheel-valve, because the wheel does not show how far the valve is opened, whilst the handle of the cock can be fitted with a graduated arc so that its position can be fixed with precision.

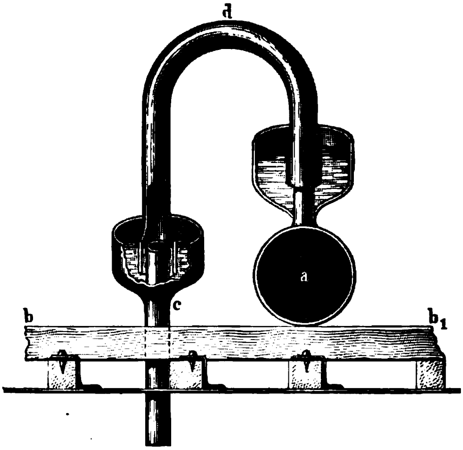
In continental works there are mostly several jets in a chamber, distributed over its length, and turned at a right angle to it or to the direction of the current of gas. This, no doubt, interferes with the draught, and in any case necessitates another, stronger steam-jet in the same direction as the draught. In England it is quite usual to employ only the latter, mostly beside, above, below, or even within the pipe conveying the gas from the burners, the Glover tower, or the preceding chamber. Some introduce the steam quite near the top, others in the centre of the chamber-end. A single steam-jet suffices, if the length of the chamber does not exceed about 130 feet; in longer chambers it would not carry right through.

Perfectly absurd is the arrangement given in every edition of Payen's 'Précis,' even up to the last one (1877), and copied from it into many other treatises. Here the steam-jets are shown partly in the chamber-bottom, coming through the chamber-acid. No practical man can imagine that this plan, if it has been actually carried out anywhere, has not been abolished at the first opportunity; for the shaking by the steam must gradually cause a leakage at the joint, which cannot be got at, owing to the chamber-floor; nor can it be repaired till the chamber has been entirely emptied.

Experience has shown that a single steam-jet from a 1-inch pipe is quite sufficient for feeding chambers up to 130 feet length, and also that the distribution of moisture through the chamber is properly effected. By arranging a single steam-jet, the cost of cocks, branches, &c. is saved, and the regulation of the supply of steam is much simpler and easier than if, for instance, four cocks were to be opened one quarter as much as the cock of the single jet.

In spite of this, many manufacturers, probably from unnecessary apprehensions, prefer introducing the steam in several places—for instance, through the chamber-top. An apparatus by which steam can be introduced at many places and yet regulated at a single place has been described by Scheurer-Kestner (Wurtz, Dict. de Chimie, iii. p. 149); it is shown in fig. 151: *a* is the copper main pipe running in the centre of the chamber-top, and held fast by the joist $b\, b_1$, as well as the branches *c*. The latter are arranged alternately on the left and right hand at distances of 16½ feet; they are made of lead, pass through the chamber-top, and are burnt into it. The arm *d*, covered with straw rope, serves for making the communication between *a* and *c*. Both pipes have hydraulic lutes, so that only a very low pressure can be employed. The main pipe, *a*, is provided with a cock, and the supply of steam regulated by this. The steam, entering the pipe at the front end of the chamber, will principally escape through the first branches, where it is most needed, because in the beginning most unchanged sulphurous acid is present. The pipe *a* has sufficient fall for emptying the condensed water. (This arrangement seems to offer no advantage over simple branches on a main pipe, and has the great disadvantage that only a very low pressure can be employed, as the water is easily thrown out of the hydraulic joints of *a* and *c*).

Fig. 151.



At the Oker Works there is also a steam-pipe extending above the chambers, from which, at intervals of 17 feet, branches of ¾-inch bore enter the latter; from these the steam issues, by several small openings immediately below the top, in several directions. The tension there is 2 atmospheres (Bräuning, *l. c.* p. 137). A similar arrangement exists at Aussig and elsewhere. In all these cases each branch-cock must be regulated separately.

The total quantity of steam required for a set of chambers, which should be known approximately in order to fix upon the boiler-space and the size of the main pipes, of course depends, first, upon the quantity of sulphur to be burnt, secondly upon the existence of a Glover tower, and thirdly upon the strength to which the acid is brought in the chambers. A general rule, therefore, cannot be laid down. The two latter conditions are partly reciprocal; the stronger the acid is made in the chambers, the less water is evaporated in the Glover tower, and *vice versâ*. If we assume, adopting a very usual proportion, that all the chamber-acid is brought up to 124° Tw., and that it is concentrated in the Glover tower up to 148° Tw., the amount of steam required will be as follows:—

Each pound of sulphur burnt requires,

1st, for forming $\frac{98}{32}SO_4H_2$, $\frac{18}{32}$ water ...... $=0·5625$ lb.

2nd, for diluting it down to 124° Tw. ($=70$ per cent. SO_4H_2), $\frac{30 \times 98}{70 \times 32}$ ...... $=1·3125$ „

1·8750 „

Of this nothing is lost with the escaping gas, as this passes in the Gay-Lussac tower through strong vitriol; on the contrary, the Glover tower saves the steam corresponding to a concentration from

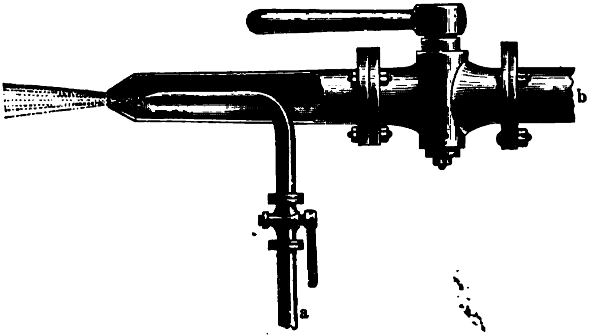
124° ($=70$ per cent.) to 148° Tw. ($=80$ per cent.), viz. $\frac{10 \times 98}{70 \times 32}$ .... $=0·4375$ lb.

Leaving................. 1·4375 lb.

which must be supplied to the chambers. To this must be added a certain quantity for water condensing in the steam-pipes; but this cannot be estimated generally, since here every thing depends upon the length of the pipes, their thickness, surroundings, &c. It is safe to say that the steam to be generated in the boiler, without a Glover tower, amounts to about 2½—with it, to about 2 times the weight of sulphur burnt.

In lieu of feeding the chambers with steam, Sprengel (patent of October 1st, 1873) proposed liquid water in the form of a fine spray. His reasons are these:—that the steam increases the volume of the gases by its heat, and consequently more chamber-space and nitre are used, which can be avoided by introducing the water in a liquid form, sufficiently divided; and that the cost of evaporation can be saved in this way. The water is itself made into a spray by the employment of steam, since a steam-jet of 30 lb. tension escapes through a platinum nozzle in the centre of a water-jet, as shown in fig. 152 (where *a* is the steam-pipe, *b* the water-pipe); but 20 lb. of steam is sufficient for converting 80 lb. of water into a mist. Such jets are arranged in the chamber-sides, at distances of 40 feet from each other, and supplied with water from a tank fixed at some height above. Sprengel assumes that two thirds of the coals can be saved in this way, instancing the works at Barking Creek, where at the same time a saving of 6½ per cent. pyrites and of 14¾ per cent. nitre is said to have been effected. At those works there was no Gay-Lussac or Glover tower. Accordingly they had not the latest improvements; and the savings mentioned can hardly be explained in any other way than that the chambers were worked too hard, and so were somewhat relieved by the spray-jet. In the case of factories working with a Glover tower, Sprengel estimates the saving in coal at a third less (Chem. News, xxxii. p. 150). Of course the water- and steam-cocks must be exactly regulated, and the two nozzles must have a particular shape, so that only a fine mist and no coarser drops shall be formed, which would at once fall to the bottom and only dilute the chamber-acid.

Fig. 152.



Sprengel's process labours under the following objections:—The spray-jet contributes next to nothing to the draught, and very little to the mixing of the gases as the steam-jets mix them; and the cooling of the chamber is easily carried too far, below the temperature of 54° C. or even 40° C. (*the minimum*), usually assumed as the most favourable for the process. Nor can it be assumed that a large chamber can in this way be so uniformly supplied with moisture as by a steam-jet; and only in the first and hottest part of the set might the spray-jet be employed with some advantage. In order to feed a chamber by spray-jets it would have to receive a number of apparatus; and the complication of work caused thereby, as well as the other drawbacks mentioned above, will not be counterbalanced by the saving of coals, which will hardly be very considerable. In fact it does not appear that Sprengel's apparatus has made much way among alkali-works.

Arrangements for producing the Draught in the Acid-chambers.

Already, when treating of the burner-gas, we have had to notice the draught which is necessary in the whole set in order to keep the process of combustion and acid-formation going; and we have seen that the hot gaseous mixture in itself contains the conditions for causing a draught, since it is much lighter than the air, and thus will always have a tendency to rise from the burners to the chambers. We have also pointed to another potent source of draught, viz. the formation of liquid sulphuric acid within the chambers from mixture of the gases, which must necessarily have an aspirating action, although not only from the burners, but from all sides.

Along with these two sources of draught furnished by the essence of the acid-making process itself, there must always be another arrangement for causing further draught, especially because otherwise the current of gas could not be turned into the required direction. In the simplest case a plain *outlet-pipe* behind or above the last chamber will suffice. The Belgian Commission of 1854 even preferred this arrangement to a chimney; and many factories work quite well in this way. But it cannot be said that the excessive draught of a chimney leads to a loss of uncondensed gas and too quick a passage through the chambers; for it is always very easy to cut off an *excess* of draught by a damper &c. in the outlet; but it is nothing like so easy to increase the draught if *insufficient*. For the latter object a special steam-pipe can be arranged which ends in a nozzle turned upwards in the current of gas, and thus causes a strong draught in the way well known and practised in locomotive engines. But then regulation is all the more called for, lest the draught should be too strong; and in the end a cheap source of draught, viz. the chimney, has been replaced by a dear one, without any gain as to constant supervision and regulation. We should accordingly always prefer a *chimney* to a steam-jet, all the more as the former will always be necessary in any case for the steam-boilers. Of course the chimney, to do its work, must be higher than the chambers.

It comes to the same thing as a chimney if the outlet-pipe fixed to the last chamber has a considerable height—for instance, 50 feet (in the south of France). Where several sets of chambers exist in the same works, it is preferable to carry them all into a common chimney, providing the connecting-pipe of each set with a contrivance for regulating the draught.

The employment of a chimney is even more advisable if, as is now the case in all well-appointed works, a Gay-Lussac tower is fixed at the end of the set. In this case the draught must be regulated with even greater care than otherwise; but there must be an excess of draught at disposal to begin with. It is also a great convenience if the "sight" necessary for checking the work of the tower (comp. Chapt. X.) can be arranged in the down-draught near the ground-level, or at least the gangway round the chambers. If there is no down-draught, but a direct top draught out of the tower, it is always necessary to mount to the top to observe the "sight." It is, however, quite possible to employ the tower itself as a chimney, if it is built with its top a good deal higher than the chambers; and this is actually done at several works.

The more recent sets of chambers at Oker, utilizing the configuration of the ground, are arranged in such a way that the burners, Glover towers, chambers, and Gay-Lussac towers rise one above the other, terrace-wise. The outlet of the whole is at a height of 62 feet above the level of the burner-grates. Drawings of this arrangement are given by Bräuning (Preuss. Zeitschr. f. Berg-, Hütten- u. Salinenwesen, 1877, table ii.). It is stated there that formerly the draught could not be made sufficient, even by connecting the Gay-Lussac towers with the boiler-chimneys; but this only proves that the latter had not the necessary excess of drawing-power. With this expensive plan, followed at Oker, there is the convenience connected of running both the chamber-acid and the Gay-Lussac acid into the Glover tower by natural fall; but the latter could only be made 17 feet high.

It has been noticed at Oker that a very long draught-pipe, connecting the last chamber with the tower, affords the advantage of neutralizing to some extent the oscillations of the outer atmospheric pressure, and thus facilitating the regulation. Be this as it may, such a long pipe, although it causes some loss of draught by friction, will always be very useful, by cooling the gas previously to entering the absorbing-tower.

We have already said something about the principles according to which the supply of air must be regulated; and we shall have to come back to this in the next Chapter. Here we must only remark that there must be in any case enough total draught *behind* the chambers, but not too much; otherwise, even if the burners themselves are protected against excess of draught by diminishing the air-holes below the grates, there is all the more tendency for air to enter the chambers from all other sides through the finest chinks and thus disturb the process. If the draught is excessive, the incubus of the vitriol-maker, pale chambers, at once makes its appearance.

Whether, therefore, the draught is produced by a chimney or by an open pipe, there must always be some contrivance for regulating

Fig. 153.

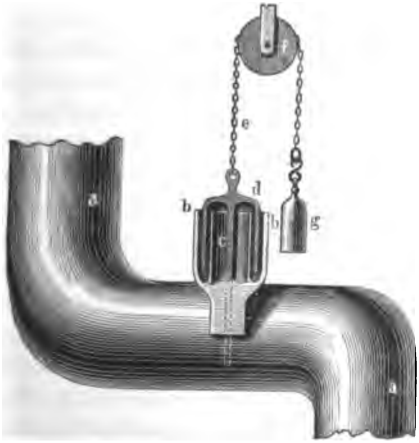
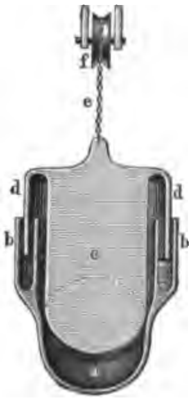


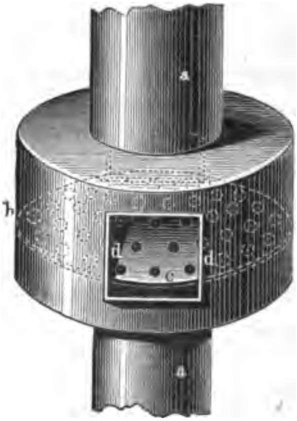
Fig. 154.



it. At many works this is done by a simple damper, introduced into the respective lead pipe by a slit, luted with clay or not at all. The arrangement shown in fig. 153, partly in elevation, partly in section, and in fig. 154, in cross section, is far more perfect. The draught-pipe, *a a*, is widened out into a rectangular vessel surrounded by a jacket, *b b*, forming an hydraulic joint; and the damper, *c*, is surrounded on all sides by the jacket *d d*, dipping into the water lute at *b*. The damper is raised and lowered by the help of the chain, pulley, and balance-weight, *e*, *f*, *g*.

In continental works the arrangement shown in fig. 155 is frequently met with. The draught-pipe, *a a*, is interrupted by a wider drum, *b*, divided into two parts by a horizontal diaphragm, *c*. The latter is perforated by a number of holes whose total area is somewhat larger than that of the pipe, *a a*. When, therefore, all the holes are open, there is no obstacle whatever for the draught; but this can be produced at will by closing a certain number of the holes with clay or lead plugs. For this purpose the space above the diaphragm is accessible by a small door, which may consist of a pane of glass, *d* (fig. 155), to which another on the other side corresponds, so that the whole at the same time serves as a "sight."

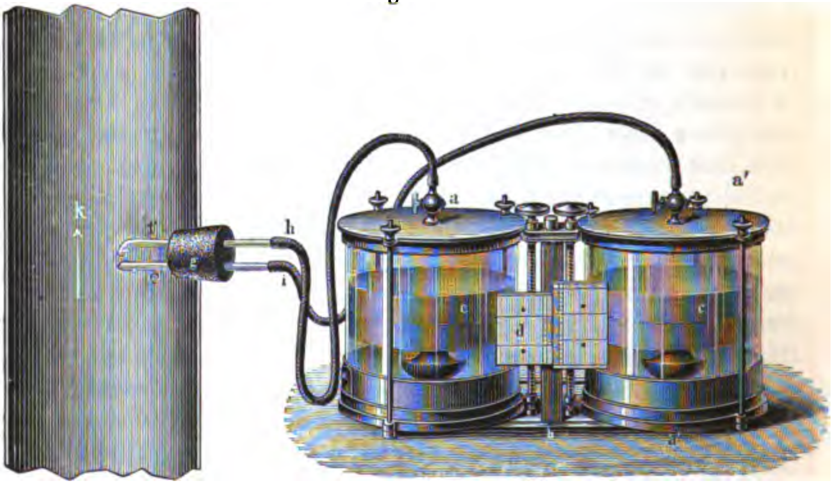
Fig. 155.



C. L. Vogt has patented (on July 29th, 1875) a peculiar contrivance for producing draught in acid-chambers, which introduces the air along with the necessary steam through a pipe with an opening of $\frac{1}{4}$ inch. The steam is under a pressure of 3 to 4 atmospheres. This invention seems to have very little object. As a rule, quite enough air enters through the burners; and in practice an excess of it is much oftener to be feared than a deficiency; only in very special cases can such an arrangement be preferable to a chimney.

Although we have in a previous Chapter excluded the use of a Combe's anemometer for regulating the access of air to the burners, because it is too delicate an instrument, and because it only shows the draught in the place which it occupies, we have here to speak of an anemometer adapted for controlling the draught in another place, viz. on leaving the chambers. This is Péclet's *differential anemometer*, as modified by Fletcher and Swan. Fletcher's modification is described in the Third Annual Report on the Alkali Act, 1863, by the Inspector, for 1866, p. 54 *et seq.*; Swan's (independently proposed by P. Hart, Chem. News, xxi. p. 200) in the 'Transactions of the Newcastle Chemical Society,' Jan. 26, 1871. Since this instrument can also be employed usefully for other purposes (as for the muriatic-acid condensers, the sulphur-recovery by Mond's process, and the chimney-draught generally), we shall here give a description of it. It is founded upon the physical principle that a current of air passing the open end of a tube causes a partial vacuum in the tube. If, therefore, a straight tube is introduced through a hole into a chimney, or into the draught-pipe taking away the chamber-gas, so that the gaseous current passes the open end of the tube at a right angle, a partial vacuum will be formed in the latter, proportionally to the velocity of the current. But the aspirating action of the chimney will be equally communicated to this tube; and we must here distinguish between these two actions. To do this, we must introduce two tubes into the chimney, one of which ends straight, whilst the other one is bent to a right angle, so that the current of air blows into it. Both tubes will now be affected by the aspirating action of the chimney; but in the straight tube this is *increased* by the aspirating action of the current crossing its open end, whilst in the bent tube it is *diminished* by the air blowing into it. The difference between the aspirating action of the two tubes is thus reducible to the action of the current of air; and by measuring it the speed of that current can be ascertained. For this purpose the two tubes are connected with a U-shaped glass tube containing water or another liquid; this will rise in one of the limbs to an extent corresponding to the difference of suction. Since the sucking-action of the chimney acts upon both limbs, it is eliminated, and the difference of level corresponds merely to the different action exerted by the current of air upon the straight tube, which it crosses, and the bent one, into which it blows. This action rises and falls with the speed of the current; and the latter accordingly can be deduced from it. Water (used by Péclet), on account of the friction exercised in the U-tube, is only adapted for currents of a greater speed than 5 feet per second. Fletcher overcame this difficulty thus:—In order to lessen the friction, he employed two cylinders, *a a'*, fig. 156, of 4 inches diameter, connected at the bottom by a narrow tube, *b*. This arrangement is ten times as sensitive as a U-tube of 0·4 inch width would be, since the area upon which the pressure acts is increased 100-fold, but the circumference upon which friction acts only 10-fold. The rising and falling of the liquid is observed by means of metal floats, *c c*, upon which a very fine horizontal line is marked by a lathe; and the scale, *d*, provided with a vernier and a very fine adjusting-screw, permits the difference of level, down to one thousandth part of an inch, to be read off. This is possible, not with water, whose mobility, owing to its adhesion to the glass, is too slight, but with *ether*, whose adhesion is only one two-thousandth of that of water. The two glass tubes, *e* and *f*, are put into the draught-pipe, *k*, by means of a cork, *g*, at right angles to the cur-

Fig. 156.



rent of gas (so that it blows into the bent tube, *f*), and are connected by elastic tubes, *h i*, with *a a'*.

It remains to ascertain the relation of the readings to the speed of the currents. In any case the pressures indicated by the anemometer must correspond to the square of the speeds, and the formula will have this shape,

$$v^2=pc,$$

where v is the speed of the gas in feet per second, p the pressure in inches as shown by the anemometer, and c a constant. In order to ascertain the value of c, Fletcher made about 100 experiments in an iron flue of 14 inches diameter and 100 feet length, one of whose ends was open, the other one connected with a high factory-chimney, the draught being exactly regulated by a damper. In the open end, by dropping sulphuric acid on a red-hot brick at certain intervals, white clouds were generated, whose arrival at the other end could be observed through two opposite holes; the time elapsed in the interval indicated the speed of the current, the anemometer being read off at the same time. Such experiments were made, by altering the damper, at speeds varying from 1 to 20 feet per second. The values of c were computed by the formula

$$c=\frac{v^2}{p},$$

and, when corrected for temperature and barometrical pressure, were found to agree exactly—viz., on the average, 25·31 for a temperature of 60° F. (=15°·5 C.) and a pressure of 30 inches (=762 millims.); therefore

$$v=\sqrt{p}\times 25{\cdot}31.$$

But, later on, Fletcher found (Fifth Annual Report on the Alkali Act, p. 63 *seq.*), by a number of experiments in three flues of different lengths, the mean value of $c=28{\cdot}50$ at 60° F. and 29·92 inches pressure (the values varied from 27·38 to 29·21), at the same time deducing a mathematical formula for it by assuming that the sucking or drawing-up force in the tube was equal to the direct force of impact of the current of air on the surface of the other limb.

Thus we have

$$v^2w=g\mathrm{P},$$

where v is the velocity of the air in feet per second,

g = gravity = 32·18 feet per second,

w = weight of a cubic foot of air at 60° F. and 29·92 inches barometric pressure = 0·076107 lb.,

P = pressure in pounds per square foot on a flat surface held at right angles to the direction of the current of air.

Let p be the height of the column of liquid driven up the tube, measured in inches, W the weight in pounds of $\frac{1}{12}$ cubic foot of this liquid. Then

$$P = pW\,;\ v^2 w = gpW\,;\ v = \sqrt{p\frac{gW}{w}}.$$

Where the liquid used is water, W = 5·20833 and $v = \sqrt{p}\,46{\cdot}92$, or $p = \frac{v^2}{0{\cdot}2202}$.

If ether of the specific gravity 0·740 be employed, and the instrument be so used that the reading is double the actual column of ether supported, then

$$v = \sqrt{\frac{p}{2}\frac{gW}{w}} = \sqrt{p}\,.\,28{\cdot}55.$$

This, as will be seen, closely agrees with the result deduced from the experimental observations.

Fletcher further deduces the following formula for corrections for any temperatures different from 60° F. (t = degrees Fahrenheit),

$$v = \sqrt{p\frac{519}{459+t}} \times 28{\cdot}55,$$

and for any variations in barometric pressure (h = inches),

$$v'' = \sqrt{p\frac{29{\cdot}92}{h}}\;28{\cdot}55,$$

or, if the velocity is to be reduced to feet of air at 29·92 inches = 760 millims. barometric pressure,

$$v = \sqrt{p\frac{h}{29{\cdot}92}} \times 28{\cdot}55.$$

The complete formula, embodying the correction for variation of temperature, and for that of barometric pressure, is therefore

$$v = \sqrt{p\frac{h}{29{\cdot}92}\cdot\frac{519}{459+t}} \times 28{\cdot}55.$$

Usually, however, it is required to know the speed of the current at the barometric pressure prevailing at the time; and then the formula is

$$v=\sqrt{p\frac{29\cdot92}{h}\times\frac{519}{459+t}}\times 28\cdot55.$$

The Table given on p. 337, for the speeds corresponding to different readings of the anemometer, is computed from the formula

$$v=\sqrt{p}\times 28\cdot55;$$

and another Table is added for correcting the variations in the temperature of the current of gas. The corrections for small variations in the barometrical pressure are usually not considerable; but they can be made by means of the above formulæ—

$$v''=\sqrt{p\frac{29\cdot92}{h}}\times 28\cdot55,$$

or

$$v=\sqrt{p\frac{h}{29\cdot92}}\times 28\cdot55.$$

If the pressure is read off in millimetres, the number 760 is everywhere substituted for 29·92; or if the readings are in millimetres and the speed in metres per second is required to be known, the constant 28·55 is converted into another, according to the formula

$$\frac{0\cdot3048}{\sqrt{25\cdot4}}\times 28\cdot55=1\cdot727;$$

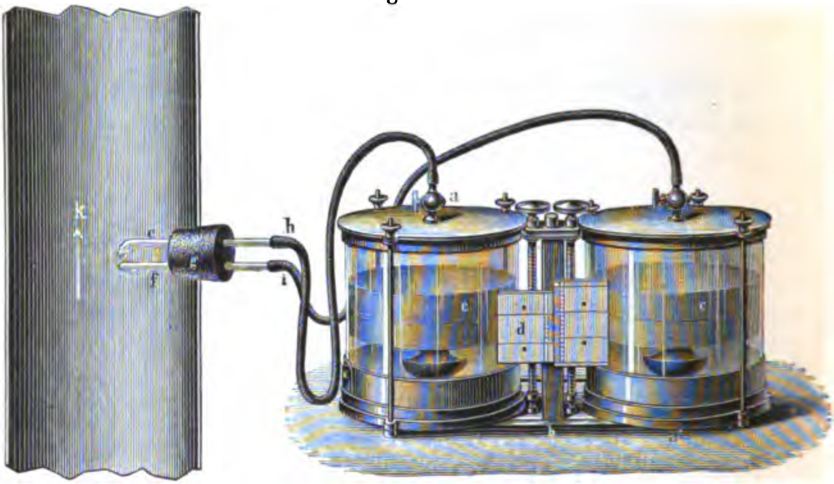
so that the formula for v' and p' in metrical measures will read $v'=1\cdot727\sqrt{p'}$.

A correction for the expansion and contraction of the ether in the instrument itself is mostly unnecessary, since it is only exposed to the ordinary temperature; it amounts to about 1 per cent. of the speeds shown in the Table for each 10° F. (=5·55° C.) deviation from 60° F.,—more for temperatures below, less for temperatures above 60° F.

In order to make the readings more exact, first the height of ether in one of the limbs is noticed, then the current is reversed by connecting the tube *e* with *a* and *f* with *a'* (fig. 157); another reading is made; and thus twice the difference of pressure caused by the suction at *f* is found. The figure thus found is read off in

Table I. and corrected for temperature by Table II. To take an instance, let the first reading be 1·039, and the second reading, after reversing the current, 0·861, the difference will be 0·178. On referring to Table I., the speed 12·05 feet per second will be found. This, however, is only true if the temperature of the air is 60° F. Should it in the case in question be 520° F., Table II. gives the correcting multiplier, 0·7280. This, multiplied by 12·05, is 8·772, the true speed of the current if measured at the temperature of 60° F.

Fig. 157.



This instrument is not influenced by soot, heat, or corrosive vapours; it can be placed at some distance from the flue to be tested, if longer elastic tubing be used; and it can, of course, be employed both for aspirating and for pressure currents (fan-blasts &c.), and as a measure for the speed of atmospheric currents.

To be sure, like every other anemometer, Fletcher's only indicates the pressure at the place occupied by its receiving portion; and accordingly the tubes *e* and *f* must be introduced so far as to reach into the air-current to the extent of about one sixth of the diameter of the flue. The velocity at this place is assumed to be nearly equal to the average; but this is very doubtful, and there are no means at present known of measuring the absolute quantities of air passing through a flue of any considerable sectional area with any degree of certainty.

Table I.—*Showing the Speed of Currents of Air as indicat*
Ether Anemometer.

$v = \sqrt{p} \times 28{\cdot}55.$

Temperature 60° Fahr. Barometer 29·92 inches

Manometer reading.	Speed of air.	Manometer reading.	Speed of air.	Manometer reading.	Spe
in.	ft. per sec.	in.	ft. per sec.	in.	ft.
0·001	0·903	0·047	6·189	0·093	
0·002	1·277	0·048	6·255	0·094	
0·003	1·564	0·049	6·320	0·095	
0·004	1·806	0·050	6·384	0·096	
0·005	2·019	0·051	6·448	0·097	
0·006	2·212	0·052	6·510	0·098	
0·007	2·389	0·053	6·572	0·099	
0·008	2·554	0·054	6·634	0·100	
0·009	2·709	0·055	6·695	0·102	
0·010	2·855	0·056	6·756	0·104	
0·011	2·994	0·057	6·816	0·106	
0·012	3·127	0·058	6·876	0·108	
0·013	3·255	0·059	6·935	0·110	
0·014	3·378	0·060	6·993	0·112	
0·015	3·497	0·061	7·051	0·114	
0·016	3·612	0·062	7·109	0·116	
0·017	3·723	0·063	7·166	0·118	
0·018	3·830	0·064	7·223	0·120	
0·019	3·935	0·065	7·279	0·122	
0·020	4·038	0·066	7·335	0·124	
0·021	4·137	0·067	7·390	0·126	
0·022	4·235	0·068	7·445	0·128	
0·023	4·330	0·069	7·500	0·130	
0·024	4·423	0·070	7·554	0·132	
0·025	4·514	0·071	7·608	0·134	
0·026	4·604	0·072	7·661	0·136	
0·027	4·691	0·073	7·713	0·138	
0·028	4·777	0·074	7·766	0·140	
0·029	4·862	0·075	7·819	0·142	
0·030	4·945	0·076	7·871	0·144	
0·031	5·027	0·077	7·922	0·146	
0·032	5·107	0·078	7·974	0·148	
0·033	5·187	0·079	8·025	0·150	
0·034	5·265	0·080	8·075	0·152	
0·035	5·342	0·081	8·125	0·154	
0·036	5·418	0·082	8·175	0·156	
0·037	5·492	0·083	8·225	0·158	
[illegible]	5·565	0·084	8·275	0·160	
[illegible]	5·638	0·085	8·324	0·162	
[illegible]	5·710	0·086	8·373	0·164	
[illegible]	5·781	0·087	8·421	0·166	
[illegible]	5·851	0·088	8·469	0·168	
[illegible]	5·921	0·089	8·517	0·170	
[illegible]	5·989	0·090	8·565	0·172	
[illegible]	6·056	0·091	8·613	0·174	
[illegible]	6·123	0·092	8·660	0·176	

Table I. (continued).

Manometer reading.	Speed of air.	Manometer reading.	Speed of air.	Manometer reading.	Speed of air.
in.	ft. per sec.	in.	ft. per sec.	in.	ft. per sec.
0·178	12·05	0·284	15·23	0·390	17·83
0·180	12·11	0·286	15·28	0·392	17·88
0·182	12·18	0·288	15·33	0·394	17·93
0·184	12·25	0·290	15·38	0·396	17·98
0·186	12·31	0·292	15·44	0·398	18·02
0·188	12·38	0·294	15·49	0·400	18·06
0·190	12·45	0·296	15·54	0·402	18·11
0·192	12·51	0·298	15·59	0·404	18·16
0·194	12·57	0·300	15·64	0·406	18·20
0·196	12·64	0·302	15·70	0·408	18·24
0·198	12·71	0·304	15·75	0·410	18·28
0·200	12·77	0·306	15·80	0·412	18·33
0·202	12·83	0·308	15·85	0·414	18·38
0·204	12·90	0·310	15·90	0·416	18·42
0·206	12·96	0·312	15·95	0·418	18·46
0·208	13·02	0·314	16·00	0·420	18·50
0·210	13·08	0·316	16·05	0·422	18·55
0·212	13·15	0·318	16·10	0·424	18·60
0·214	13·21	0·320	16·15	0·426	18·64
0·216	13·27	0·322	16·20	0·428	18·68
0·218	13·33	0·324	16·25	0·430	18·72
0·220	13·39	0·326	16·30	0·432	18·77
0·222	13·45	0·328	16·35	0·434	18·82
0·224	13·51	0·330	16·40	0·436	18·86
0·226	13·57	0·332	16·45	0·438	18·90
0·228	13·63	0·334	16·50	0·440	18·94
0·230	13·70	0·336	16·55	0·442	18·99
0·232	13·76	0·338	16·60	0·444	19·03
0·234	13·82	0·340	16·65	0·446	19·07
0·236	13·88	0·342	16·70	0·448	19·11
0·238	13·94	0·344	16·75	0·450	19·15
0·240	13·99	0·346	16·80	0·452	19·20
0·242	14·05	0·348	16·85	0·454	19·24
0·244	14·11	0·350	16·89	0·456	19·28
0·246	14·17	0·352	16·94	0·458	19·32
0·248	14·23	0·354	16·99	0·460	19·36
0·250	14·28	0·356	17·04	0·462	19·41
0·252	14·34	0·358	17·09	0·464	19·45
0·254	14·40	0·360	17·13	0·466	19·49
0·256	14·45	0·362	17·18	0·468	19·53
0·258	14·50	0·364	17·23	0·470	19·57
0·260	14·56	0·366	17·28	0·472	19·62
0·262	14·62	0·368	17·33	0·474	19·66
0·264	14·68	0·370	17·37	0·476	19·70
0·266	14·74	0·372	17·42	0·478	19·74
0·268	14·79	0·374	17·47	0·480	19·78
0·270	14·84	0·376	17·52	0·482	19·82
0·272	14·90	0·378	17·56	0·484	19·86
0·274	14·96	0·380	17·60	0·486	19·90
0·276	15·01	0·382	17·65	0·488	19·94
0·278	15·06	0·384	17·70	0·490	19·98
0·280	15·11	0·386	17·75	0·492	20·02
0·282	15·17	0·388	17·79	0·494	20·06

Table I. (continued).

Manometer reading.	Speed of air.	Manometer reading.	Speed of air.	Manometer reading.	Speed of air.
in.	ft. per sec.	in.	ft. per sec.	in.	ft. per sec.
0·496	20·10	0·590	21·94	0·700	23·89
0·498	20·14	0·600	22·12	0·750	24·73
0·500	20·18	0·610	22·30	0·800	25·54
0·510	20·38	0·620	22·48	0·850	26·32
0·520	20·58	0·630	22·66	0·900	27·08
0·530	20·78	0·640	22·84	0·950	27·83
0·540	20·98	0·650	23·02	1·000	28·55
0·550	21·17	0·660	23·20	1·250	31·93
0·560	21·37	0·670	23·38	1·500	34·97
0·570	21·56	0·680	23·55	1·750	37·77
0·580	21·75	0·690	23·72	2·000	40·37

Table II.—*Showing the Values of* $\sqrt{\frac{519}{459+t}}$ *for Values of t from* 0 *to* 1000; *or Corrections for Temperature.*

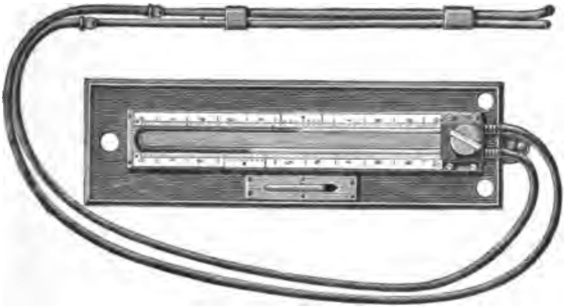
t, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$	t, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$	t, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$
0	1·0634	130	0·9388	260	0·8497
5	1·0577	135	0·9348	265	0·8467
10	1·0520	140	0·9309	270	0·8438
15	1·0464	145	0·9270	275	0·8409
20	1·0409	150	0·9232	280	0·8380
25	1·0355	155	0·9194	285	0·8352
30	1·0302	160	0·9156	290	0·8324
35	1·0250	165	0·9119	295	0·8296
40	1·0198	170	0·9083	300	0·8269
45	1·0148	175	0 9047	305	0·8242
50	1·0098	180	0·9012	310	0·8215
55	1·0049	185	0·8977	315	0·8189
60	1·0000	190	0·8943	320	0·8163
65	0·9952	195	0·8909	325	0·8137
70	0·9905	200	0·8875	330	0·8111
75	0·9858	205	0·8841	335	0·8085
80	0·9812	210	0·8808	340	0·8060
85	0·9767	215	0·8775	345	0·8035
90	0·9723	220	0·8743	350	0·8010
95	0·9679	225	0·8711	355	0·7985
100	0·9636	230	0·8680	360	0·7960
105	0·9593	235	0·8649	365	0·7936
110	0·9551	240	0·8618	370	0·7912
115	0·9509	245	0·8587	375	0·7888
120	0·9468	250	0·8557	380	0·7865
125	0·9428	255	0·8527	385	0·7842

TABLE II. (continued).

t, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$	t, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$	t, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$
390	0·7819	595	0·7017	800	0·6420
395	0·7786	600	0·7000	805	0·6407
400	0·7763	605	0·6983	810	0·6395
405	0·7741	610	0·6967	815	0·6382
410	0·7729	615	0·6951	820	0·6369
415	0·7707	620	0·6935	825	0·6357
420	0·7685	625	0·6919	830	0·6345
425	0·7663	630	0·6903	835	0·6333
430	0·7641	635	0·6887	840	0·6321
435	0·7619	640	0·6871	845	0·6309
440	0·7598	645	0·6856	850	0·6297
445	0·7577	650	0·6841	855	0·6285
450	0·7556	655	0·6826	860	0·6273
455	0·7535	660	0·6811	865	0·6261
460	0·7514	665	0·6796	870	0·6249
465	0·7494	670	0·6781	875	0·6237
470	0·7474	675	0·6766	880	0·6225
475	0·7454	680	0·6751	885	0·6214
480	0·7434	685	0·6736	890	0·6203
485	0·7414	690	0·6721	895	0·6192
490	0·7394	695	0·6706	900	0·6181
495	0·7375	700	0·6691	905	0·6169
500	0·7356	705	0·6676	910	0·6158
505	0·7337	710	0·6662	915	0·6147
510	0·7318	715	0·6648	920	0·6136
515	0·7299	720	0·6634	925	0·6125
520	0·7280	725	0·6620	930	0·6114
525	0·7261	730	0·6606	935	0·6103
530	0·7243	735	0·6592	940	0·6092
535	0·7225	740	0·6578	945	0·6081
540	0·7207	745	0·6565	950	0·6070
545	0·7189	750	0·6552	955	0·6059
550	0·7171	755	0·6538	960	0·6048
555	0·7153	760	0·6524	965	0·6037
560	0·7137	765	0·6511	970	0·6026
565	0·7119	770	0·6498	975	0·6015
570	0·7102	775	0·6485	980	0·6004
575	0·7085	780	0·6472	985	0·5994
580	0·7068	785	0·6459	990	0·5984
585	0·7051	790	0·6446	995	0·5974
590	0·7034	795	0·6433	1000	0·5964

Fletcher's anemometer has been improved by Swan in the following way. In lieu of the 4-inch cylinders he takes a U-tube of $\frac{1}{8}$ inch diameter, narrowed in the bend to diminish the oscillations. The tube is 10 inches long, and placed with an inclination of 1 in 10; each limb has a scale and vernier, the latter partly made of glass and covering at the same time the scale and the tube, so that it is easy to read off to $\frac{1}{100}$ inch. The ends of the tube are connected with a two-way cock, so that the current can be reversed without opening any joint. Fig. 158 shows the instrument as seen from above, so that its inclination to the vertical line does not appear. It is fixed on a stand provided with a spirit-level and adjusting-screws. It is employed just like Fletcher's anemometer; but, owing to the inclination of 1 in 10, the column of ether in the tube occupies ten times the space corresponding to its height, and the reading to $\frac{1}{100}$ inch gives thus the same result as the very difficult one to $\frac{1}{1000}$ inch in Fletcher's instrument. The narrowness of the tubes does not matter in the case of ether, as the friction may be entirely neglected with this substance (recently Fletcher himself has come back to ordinary U-tubes, giving up the cylinders and floats). Swan's anemometer must always be placed exactly level in the direction of its length; but it need not be levelled across, if a reading be made in one limb, the two-way cock turned, and the new reading in the same limb subtracted from the first; thus it is unnecessary to read off at both limbs, which would involve levelling across as well. The speeds are found from Fletcher's table, dividing the readings by 10.

Fig. 158.



Other instruments for measuring the draught are, for instance, those of Kretz (Dingl. Journ. cxc. p. 16), of Ramsbottom (ib. clxxx. p. 334), of Scheurer-Kestner (ib. ccvi. p. 448 and ccxxi. p. 427), none of which can vie with Fletcher's in sensitiveness. The very ingenious anemometer of Hurter (Dingl. Journ. ccxxix. p. 160) is only adapted for laboratory use.

CHAPTER IX.

THE CHAMBER-PROCESS.

In order to *start a set of chambers*, first of all its bottom must be covered with acid. This is absolutely necessary when the sides are not burnt to the bottom, but hang loosely down into its upstand, as here an hydraulic lute is required to keep the gas within the chamber. Enough liquid for the sides just to to dip into it is sufficient; for as the lead expands on the chamber getting warm, and as the liquid constantly increases by condensation, the hydraulic lute is constantly improving. However, for reasons to be stated hereafter, it will be preferred to make the depth of acid as great as possible from the outset. Only in an extreme case ought *water* to be taken for luting the chamber; acid should rather be bought elsewhere at some expense to avoid this. If it can be done, the proper thing is to take the bottom-acid at once about 90° Tw. strong. If this cannot be done, this strength ought at least to be approached as nearly as possible. The reason why starting a chamber with water or very weak acid should be avoided is, that otherwise the vapour of nitric acid dissolves in the bottom-liquid and acts upon the lead. Even if all the nitric acid were decomposed by sulphurous acid, from the hyponitric acid in contact with water nitric acid (along with nitrous acid) would be regenerated and the lead acted upon; and nitrous acid itself in contact with water decomposes with formation of nitric acid.

Quite apart from this action on the lead, starting the chambers with water causes great loss in the beginning, because the chamber-process only goes on properly when there is an abundant quantity of pretty strong acid at the bottom of the chambers. If the sides are burnt to the bottom, it is even preferable to start a chamber dry to starting it with water; but otherwise a layer of about 4 inches of acid on the bottom of such chambers is preferred.

Supposing the chambers to be luted with acid, and the burners to be heated up so that they can be charged, the connexion between them and the chambers is made and the burner-gas allowed to enter. Of course sufficient draught is given, and nitric acid admitted at once, but at first no steam, in order not to dilute the bottom-acid too much. The nitric acid is introduced precisely in the same way as later on, either in the gaseous or liquid form. At first about three or four times as much is put in as is necessary afterwards, because there must be a stock of nitre-gas collected in the chambers, which afterwards needs only to be renewed so far as any loss is suffered. Liquid nitric acid can be introduced much more quickly than gaseous, since the latter depends upon the heat of the burner-gas working the nitre-oven; but with liquid acid the thing must not be overdone, since it might not be decomposed on the cascades &c., and arrive as such at the bottom. At the beginning from 12 to 15 parts of nitrate of soda, or a corresponding quantity of nitric acid, will be employed to 100 parts of sulphur; and this will be continued till the last chamber turns yellow; then the quantity is gradually diminished till the proper point is reached.

MacCulloch (Chem. News, xxvii. p. 136) prescribes starting chambers by admitting steam and nitre-gas from the steam column (comp. the next Chapter) for five or six hours before the burner-gas is admitted. In that case, he says, the chamber works well from the first, and in one instance showed acid of 1·65 at the drips already in 12 hours. This may be so; but that process, while saving a little time and possibly a little nitre, from the outset detracts much from the durability of the chambers, since during the five or six hours when they receive only steam and nitre-gas very much nitric acid must condense, and whatever is gained by the drips is again lost by the previous dilution of the bottom-acid.

As soon as the drips and test-plugs prove that sulphuric acid is already forming in the chamber, steam is admitted, usually on the second day, but at first with much caution. Then all the factors of vitriol-making are at work, and the same rules are now valid as for the ordinary process. If every thing is in proper order, and if plenty of nitre is used (none of which, with a Gay-Lussac tower, is lost), a chamber may be in regular working order on the fourth, sometimes even on the third day after starting.

The object of a *regular chamber-process* is of course this:—to make from a given quantity of brimstone or pyrites the greatest possible quantity of sulphuric acid with the smallest possible consumption of nitre. We may add at once, as less decisive, but still of importance, to make the chamber-acid as strong as is compatible with the two conditions just stated and with a saving of the chamber-lead. In order to attain that object, the attention of the chamber-manager must be directed to many points, some of which have already been treated of in detail, whilst others must be enlarged upon here.

1st. *Complete Combustion of the Sulphur-ore.*—This, with brimstone, follows as a matter of course; with pyrites it is much more difficult (compare about this p. 172 *et seq.*).

2nd. *Proper Composition of the Burner-gas.*—This also has been treated of in the 7th Chapter; and we will here merely repeat that the proper composition of the burner-gas almost entirely depends upon the proper regulation of the draught. We have already seen (p. 179) that, apart from chemical analysis, there are practical tests to show at the burners whether the draught is right or not. But at the chambers themselves this must equally be looked to, by means of the man-lids in the top, or the test-plugs (p. 301), or by manometers or anemometers (pp. 301 and 322). Generally, the following rules can be laid down:—

In a set of three chambers the first chamber should show an outward pressure, and, accordingly, the gas should issue in force whenever a plug is opened. In the middle chamber the gas should be pretty nearly in equilibrium with the outer air; in any case there should be rather a little outward pressure than any inward suction. In the last chamber there should be some, but very little, inward suction; and behind it, but before the damper, the suction should be very perceptible. Knapp compares the chambers to a lake traversed by a river: the speed of current at its inlet is diminished in the interior of the wide basin to an insensible point; but at the outlet in the narrow draught-pipe it again comes out with the same strength as at first. Payen's 'Précis' (i. p. 318) states the speed of the gas within the chambers to be 8 to 10 inches per minute.

Generally, it may be said that the draught must be sufficient to obtain a proper working of the burners and proper composition of the gas, but *no more than this*. In England this has nearly always (down to the most recent period at least) been observed merely by practical indications, in Germany quite as generally by gas-analysis; and the rule given can here be stated more precisely in this form:—There is so much draught given that the burner-gas from brimstone approaches a percentage of 11 per cent., that from pyrites 8·5 per cent. SO_2, as far as circumstances permit, and that the gas issuing at the end still contains 5 or, better, 6 per cent. of oxygen.

Too much draught causes, with brimstone, a sublimation of the same; with pyrites also too rapid a combustion, and consequently a formation of scars. If very high, it produces cooling by the inert excess of air, also poor gas, defective utilization of the chamber-space, aspiration of air through all chinks of the chambers, carrying away of sulphurous acid and of nitrogen oxides.

Insufficient draught causes the burners to become too hot, the formation of scars, incomplete burning of the ore (and consequently again poor gas), blowing out of the burners, connecting-pipes, and chambers from all crevices (especially when any working-doors are opened), insufficient oxidation of sulphurous acid within the chambers, and escape of nitre-gas because the oxygen for forming absorbable nitrogen oxides is not present.

Either causes (as a consequence of the above) a bad yield of vitriol, large consumption of nitre, escape of sulphurous acid into the air. Further proof is not required to show the importance of regulating the draught as accurately as possible.

In the case of poor ores, and those the sulphur of which is not readily given off, also in the case of burners admitting too much false air, such as the old Belgian burners, too much air gets into the chambers, and the yield is consequently always very bad. At Oker, for instance, in 1859, from a 50-per-cent. pyrites only 100 instead of 300 per cent. of strong vitriol was obtained, with a consumption of 14·4 parts of nitre to 100 sulphur (Knocke, in Wagner's Jahresb. 1859, p. 148); and the Belgian Commission states, for the four works examined, the yield =242, 237, 259, and 238 parts, instead of 306 as required by theory. They were able to detect in the escaping gas 0·38 to 1·26 per cent. of sulphurous acid, and 11·7 to 17·4 per cent. of free oxygen.

The *regulation of the steam* is one of the most important parts of chamber-management, and should always be taken in hand by the superintendent himself, especially if the tension in the steam-boiler is kept nearly equal: of course a registering steam-gauge (p. 321) affords much greater security. The round of the chambers should be made two or three times a day; at some works it is made once every other hour. The indicator for the admission of steam is the strength of acid from the drips (p. 299), and that of the bottom-acid, taken from the place where it is strongest (that is, just opposite to the inlet from the next chamber). The two are never identical; the drip-acid is always several degrees stronger than the bottom-acid, but mostly in about the same proportion. The steam ought to be regulated so that the bottom-acid in the first chamber does not exceed 124° Tw. in strength; 128° is too much. Below 120° it is not necessary to go, although it was formerly quite general in continental works, and is still a very common rule, especially in German works, not to make the acid in the "large chamber" stronger than 106°, or at most 113° Tw. The "large chamber" corresponds to the first chamber of the English system, which likewise receives all the acid made by all the other chambers, and in which also by far the largest portion of the acid-making process is going on, even when it is followed by several other chambers. It therefore requires much more steam than the others. If a Glover tower is present, it also receives all the steam generated in this; but it requires in every case a separate steam-jet, about whose introduction p. 322 should be compared. It has been proved by manifold and long experience that the process goes on quite normally, and a maximum of acid is made, and that also the chamber-acid retains no nitrogen compounds, if the strength in the first chamber does not exceed 124° Tw. It may be said that the continental usage of making the acid only 106° to 113° Tw. means simply a waste of steam and a greater tax upon the concentrating-apparatus, without any advantage to make up for this.

The *drips* in the first chamber ought generally not to exceed 132° to 136°; but even 144° is sometimes reached without any harm to the yield or to the chambers.

P. W. Hofmann has proposed a very different procedure from the usual one (Deutsch. chem. Ges. Ber. iii. p. 5), based upon the fact that sulphurous acid conducted into sulphuric acid of 1·70 containing much nitric acid forms "chamber-crystals" ($SO_2OH . NO_2$), but no nitrous oxide (N_2O); but in the case of more dilute acid, say of 1·50, much N_2O is formed. Hofmann explains this (somewhat doubtful) fact thus, that in the latter case no concentrated vitriol is present which could form chamber-crystals. He consequently in his first chamber (which was only a tambour of 3500 cub. feet capacity) diminished the steam to such an extent that only vitriol of 1·7 was produced; and he found that now much less nitre was required for the same weight of vitriol. By always bringing up the strength of the chamber-acid to 1·7 when it had fallen below this, by means of acid of 170° Tw., he obtained a saving of 1 lb. of nitric acid to 100 lb. of sulphur.

Of course in this case the strong nitrous vitriol was not drawn off for use, but run into the next weaker chamber, where it gave up its nitre on dilution (Spence, Chem. News, xxi. p. 132; Hofmann, ibid. p. 164). Spence proposed as an improvement (ibid. p. 189) rather to keep the second and third chamber at a strength of 1·715, in order to condense the nitre-gas by Hofmann's plan, and to run the vitriol charged with nitre to the first chamber, which is amply supplied with steam, and where the nitre would again be given off for further utilization. This, no doubt, is the most rational way of carrying out Hofmann's proposal; but it never seems to have struck Spence that in this way his second and third chambers were simply used in lieu of a Gay-Lussac tower, his first in lieu of a denitrating apparatus, thus losing active chamber-space without attaining any thing like the saving of nitre possible with proper apparatus. Spence mentions that by his plan he only used 60 cwt. of nitre per week in lieu of 82 cwt.; but from his own figures Hewett proves (Chem. News, xxi. p. 200) that he formerly had used the enormous quantity of 12 per cent. of nitre to the sulphur, and that thus even the crude system of nitre-recovery inherent in his plan could not but effect a certain saving. Spence himself, later on (ibid. p. 224), expresses himself very doubtfully about the value of Hofmann's plan; and nothing further has been heard of it.

The injurious action upon the lead apprehended by Gibbins (ibid. p. 132) is contradicted by Hofmann (ibid. p. 164). So long as it is not known with what positive consumption of nitre and what yield of vitriol Hofmann has been working, nothing can be made of the alleged saving of 1 per cent. of nitre. Since the general introduction of Gay-Lussac and Glover towers his plan, anyhow, has lost any importance it may have possessed.

The acid in the *second chamber* of a set, or the middle portion of a large single chamber, ought not to be much weaker than that in the first chamber, if a Gay-Lussac tower is present. In a set of three chambers the second should, on an average, show 116° Tw.; with four chambers 120° may be assumed for the second, and 113° Tw. for the third. If, however, no nitre-recovery is practised, the middle chambers of a set average only 77° to 90° Tw. The steam is regulated accordingly. The drips will show from 10° to 15° Tw. more than the bottom-acid.

The strength of the acid in the *last chamber*, or the last portion of a single chamber, differs even to a greater extent, according to whether the work is done with or without a Gay-Lussac tower. In the former case the rule can be laid down that this chamber ought not to fall below 106° Tw. A few degrees less do not do any great harm; but it is always best to go up to that strength, since the gas ought to enter the tower as cool and dry as possible. If the strength falls below 78°, or at most to 70°, the chamber-acid begins to contain much nitric acid instead of nitrous acid; and there is then danger for the lead. Sometimes, for fear of this, acid is pumped into the last chamber from the first. In the absence of a Gay-Lussac tower, where there is little nitre in the last chamber, the strength of the acid is allowed to fall to 52°, in some works even to 42° or even 32° Tw. This is done in order to keep the nitrogen oxides back as nitric acid, but with evident danger to the chamber-lead. For this reason some manufacturers, even without a Gay-Lussac tower, keep the last chamber stronger, from 77° to 106° Tw. In the south of France the usual strength is 72° to 77° Tw. (Favre, Monit. Scientif. 1876, p. 273).

We have already calculated the absolute quantity of steam which has to be generated for chamber-work (p. 324). We have seen that, in order to form chamber-acid, we must introduce steam to the amount of about two and a half times the weight of sulphur in the pyrites. The question is now, how much of this in the atmosphere of the chamber can exist as vapour, and how much must be condensed to liquid water, since it is of great importance that no real precipitation of water, as such, should take place, which would condense nitric acid and dilute the vitriol. In the formula (p. 236),

$$V' = \frac{(273+t)V \times 760}{273\,(b-e)},$$

e signifies the tension of vapour at the temperature t° C. Now we have seen before (p. 236) that for each kilog. of sulphur burnt 6199 litres of air, at 0° and 760 millims. tension, whose volume is not changed by the formation of sulphurous acid, has to be introduced into the chambers. At a temperature of 50° C. the tension of watery vapour is equal to 92 millims. mercury; and by introducing these values into the above formula we get

$$\frac{(273+50)\,6199\,.\,760}{273\,(760-92)}=8345 \text{ litres,}$$

which are filled with aqueous vapour of 92 millims. and gas of 668 millims. tension. Now 1 litre of aqueous vapour at 0° and 760 millims. tension weighs 0·804343 gram, and at 50° and 92 millims. tension it must be

$$=\frac{(273+50)\,760}{273\,.\,92}=9{\cdot}7739 \text{ litres.}$$

From the proportion 9·7739 : 0·804343 :: 8345 : x we have

$$x=686{\cdot}8 \text{ grams.}$$

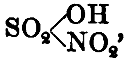
Accordingly the steam which the gas introduced for each kilog. of sulphur, occupying at 50° and 760 millims. tension a volume of 8345 litres, can hold as such, only amounts to 0·6868 kilog., whilst the total amount of water needed is 2·5 kilog., or nearly four times as much. The three fourths of the total amount of steam introduced into the chambers must accordingly be condensed to water in the atmosphere of the chamber; but this is not done at once in the form of drops, but in that of a fine mist spreading all over the chamber, and probably assisting in this state the process of formation of sulphuric acid. It is not known what quantity of water can exist in such a state of mist suspended in the gas.

If the chambers receive *too much steam,* the acid in them is diluted too much to begin with. But in the first and second chamber a more serious drawback follows: the nitrogen acids are mostly withdrawn from the *atmosphere* of the chamber, and are precipitated in a liquid form upon the chamber-*bottom,* where they can very little assist the acid-forming process, and, moreover, act upon the lead. So long as the bottom-acid is pretty strong (say, up to 90°), it will not long keep the nitric acid, but again give it off as lower nitrogen oxides by the action of sulphurous acid; but if the excessive supply of steam continues, it will soon keep the nitric acid back; and as the process is thereby disturbed, even the steam which should have been used up in the formation of sulphuric acid is condensed to water, and the dilution of the bottom-acid thus again increased. If this state has once set in, it is not always easily remedied. Cutting off the steam is not sufficient; much more nitre must be put in as well; and yet the bottom-acid only gradually gets up to its normal strength. In the mean time the yield falls off, the consumption of nitre increases very much, and the action on the chamber-lead does permanent damage. Thus it is apparent that an excess of steam does very much harm; and great care must be taken lest the strength of the acid should go down below the proper amount. The chambers soon show when they have too much steam by getting pale. A pale chamber often gets red again in an hour after the supply of steam has been partially cut off.

An excess of steam has another injurious consequence, which can only be explained in detail when treating of the theory of the chamber-process, viz. the formation of nitrous oxide, or even of nitrogen, whilst the reduction of the nitrogen-acids ought not to go beyond nitric oxide. Neither nitrous oxide nor nitrogen can be reoxidized to nitrogen-acids; but they escape with the other gas, and thus cause a loss of nitre. Their formation takes place according to these equations:—

$$2\,SO_2+N_2O_3+2\,H_2O=2\,SO_2(OH)_2+N_2O\,;$$
$$3\,SO_2+N_2O_3+3\,H_2O=3\,SO_2(OH)_2+2\,N.$$

Nor will the process go on normally if the chambers receive *too little steam.* Then from the sulphuric and nitrous acids a compound is formed, which we shall afterwards describe in detail, formerly known as "chamber-crystals," now as "nitrosulphonic acid," or "nitrosyl sulphate," of the formula



$$SO_2\!\left<\begin{matrix}OH\\NO_2\end{matrix}\right.,$$

according to this reaction:—

$$SO_2(OH)_2+NO\,.\,OH=SO_2(OH)\,(NO_2)+HOH.$$

It rarely happens in actual practice that there is so little water present that chamber-crystals can occur in the solid state; in the connecting-pipes this happens more frequently. But a solution of the same may very easily be formed in the bottom-acid as soon as the latter becomes too strong. With the strength assumed by us as normal for the first chamber, viz. 124° Tw., the acid can easily keep chamber-crystals in solution, and show the reactions of nitrous acid; and care must accordingly be taken that the conditions for the formation of nitrosulphonic acid are not present in the chamber-air. For this it is essential that there should be enough water present, best of all as steam. In this case nitrosulphonic acid is always decomposed, according to the usual explanation, thus :—

$$SO_2(OH)(NO_2)+H_2O=SO_2(OH)_2+NO.OH.$$

It thus does not get into the bottom-acid in a liquid state. When once, however, it has got into this, a much larger dilution is required for again decomposing the compound than is admissible on other grounds, and consequently a loss of nitre will be suffered with the vitriol drawn off from the first chamber for use. Where all the chamber-acid passes through the Glover tower and is denitrated there, only this disadvantage remains, that the nitrous acid present in a solid or liquid form as nitrosulphonic acid is withdrawn from the chamber-process until this compound is decomposed by turning on more steam.

A deficiency of steam also acts in this way, that the vitriol becomes too concentrated, and may thus to some extent act upon the lead. So long as the strength of the chamber-acid does not exceed 144° (and this will very rarely happen, even with faulty management), the harm is not much. For very good reasons, the last chamber, if a Gay-Lussac tower is present, receives very little steam, the case of smaller chambers (tambours) none at all. But this may be carried too far; and then, in spite of the dark-red appearance of the chambers, there is a bad yield of vitriol, because the water necessary for its formation is missing, and SO_2 and O go away uncombined. This occurs especially when the chamber appears of a very clear, transparent red, instead of being somewhat dim and misty.

On the whole, it is evident that the risks run by a deficiency of steam are nothing like so serious as those arising from an excess of steam.

The *supply of nitre* must be regulated on entirely different principles, according to whether there is an apparatus for the recovery of nitre or nŏt. In the latter case care must be taken not to have too much nitre-gas in the last chamber; for every thing issuing from it is a total loss. Therefore the last chamber but one is kept strongly yellow or red, in order to advance the acid-forming process, but the last chamber only faintly yellow.

The bottom-acid in the latter, which is usually kept at 52° Tw., or even below, will partly absorb the nitre-gas as nitric acid, and there will not be so much of it lost. This state of the last chamber is attained by giving it much steam; but it will be seen at once that in this chamber very little work can be done unless a very large loss of nitre is suffered; for only if the latter be present in large quantity will the oxidation of sulphurous acid go on all through the chamber. Therefore one of these two things must be done: either a large quantity of nitre must be sacrificed in order to utilize the last chamber (say, 12 per cent. of the sulphur, or *four* times as much as with a Gay-Lussac tower), or the last chamber is practically used only for recovering part of the nitre; thus actually a third or a fourth of the chamber-space is sacrificed, and so much less sulphur can be burnt in that set. For all that, the last chamber is not merely a costly but also a very inefficient apparatus for recovering the nitre; even if used as such, very little below 10 per cent., mostly above 10 per cent., of nitre to the sulphur must be employed in order to get a good yield. With poor, badly burning ores, of course, even more nitre is consumed, corresponding to the excess of air.

These considerations will make it evident how much more rational it is to *recover the nitre* by a proper apparatus. By this there is a saving of a fourth, up to a third, in chamber-space, at least one of two thirds in nitre, and mostly also better yield, because up to the last an excess of nitrous gas is present, and no sulphurous acid can escape oxidation by it. In this way any escape of noxious vapours is also much more completely prevented. The construction of the nitre-recovery apparatus, and every thing pertaining thereto, will be described in the next Chapter. Here we shall only describe the way of managing the chambers themselves in this case. Supposing the set to consist of three chambers (the reader will easily reduce this to any other proportion by analogy), the first chamber into which, in any case, both the gas from fresh nitric acid and that from the nitrous vitriol are introduced, whether it be by nitre-ovens, or cascades, or Glover towers, or steam-columns, will always have an excess of nitre-gas. In spite of this the characteristic yellow and red colours of nitrous and hyponitric acids in the gaseous state will not be perceived in the first chamber, both because the sulphurous acid, likewise present in excess, constantly reduces most of the nitrous and hyponitric acids to colourless nitric oxide; and because the formation of sulphuric acid, principally going on in this chamber, generates in large quantities the well-known heavy white clouds. The whole atmosphere of the chamber is filled with these, and, owing to its opacity, its colour cannot be clearly recognized. In the second chamber the atmosphere is already much clearer; and as also there is very much less sulphurous acid present, a portion of the higher nitrogen oxides will be perceived by their peculiar colour. There is, however, still so much sulphurous acid present, that the mixture of gases in the second chamber will only show a more or less reddish yellow.

In the third chamber, however (in a set of more chambers, in the last—in a single chamber, in its last portion), the nitre-gas should largely predominate. There ought to be very little sulphurous acid here; and before the gas issues out of the chamber into the absorbing-tower, the sulphurous acid ought to be entirely removed from it. This is only possible by a large excess of nitrogen acids; and as, according to previous explanations, there is also oxygen present (5 to 6 per cent. by volume), that excess will not exist as colourless nitric oxide, but as nitrous and hyponitric acids. This is proved by the last chamber showing a dark-red colour, sometimes so deep as to be opaque. Even in the much shallower layer of gas seen in the "sight" of the pipe leading to the absorbing-tower, the red colour ought to be quite decided. Within the chamber the red ought to be not quite transparent, but dimmed by a mist of water (comp. p. 351).

The *colour of a chamber* can be observed by opening the man-lids on the top or the clay plugs in its side, but in a much more convenient and accurate way by glass windows put in the sides of the chamber itself (as described, p. 302). As soon as the last chamber gets paler, the cause of this must be sought for. It may be that it has got too much or too little steam or too little nitre; but it is always a sign that something is wrong; and, by comparing the other symptoms, especially the strength and the nitrosity of the drips and bottom-acids, the special cause of the fault must be got at. When the last chamber becomes quite pale, it is certain that a great loss is suffered by sulphurous acid escaping from it; and the latter, on its way through the Gay-Lussac tower, will even denitrate the nitrous vitriol contained in the latter, and cause a loss of nitre in the shape of nitric oxide escaping into the outer air. Every thing must therefore be done to avert the above phenomenon.

Apart from the colour, the gradual diminution of sulphurous acid and increase of nitrogen acids in the chamber-gas as it proceeds on its way can be perceived from other signs, such as the *smell* and the *chemical analysis* of the gas. The judgment by smell is so much more uncertain and inexact than that by colour that it is not worth while to enter upon it in detail. A chemical analysis of the gas would certainly permit the reaction in the individual chambers to be traced with ease and safety; but this plan is not usual, and even the best continental works only make two gas-analyses—that of the burner-gas before entering the chambers, and that of the gas finally leaving the apparatus as it issues from the Gay-Lussac tower. It would give some little trouble to analyze the chamber-gas between as well; nor is this necessary, since its colour gives a sufficient indication for the purpose in question.

Along with testing the *chamber-acid* for its strength, it is of great importance to test it also for its *nitrosity* (percentage of nitrogen acids); and this forms a necessary complement to the observation of the colour of the chambers. Under normal circumstances the percentages of nitrous acid (or rather of nitrosyl sulphate) and of nitric acid in the chamber-acid are so small that its quantitative estimation by the usual method is very inaccurate, especially because a number of impurities interfere with the accuracy of the process. In practice, however, a simple and momentarily made colorimetrical test with ferrous sulphate is sufficient for the object in question.

When a solution of ferrous sulphate is poured upon the drip- or chamber-acid contained in a test-tube so that the liquids are not mixed, a yellow ring is formed at the point of contact, if traces of the higher nitrogen oxides are present. With more nitrogen oxides the ring becomes darker; with still more the whole ferrous sulphate solution assumes a deep brown or black colour. In this case effervescence readily sets in, the liquid getting hot, and the dissolved nitric oxide, with the black colour, being driven off by the heat. With some practice, and always working exactly in the same way, it is quite possible to get a good idea of the percentage of nitre in the chamber-acid by its appearance under the above conditions. The testing for a set of four chambers can be carried out in this way:—A stand containing eight ordinary test-tubes of 5 inches height is once or, preferably, twice a day taken to the chambers, and the tubes filled up to about 4 inches with samples of the drip- and bottom-acids of each chamber; at the same time the strength of each sample is taken by the hydrometer, and written on the stand at the bottom of each tube. The acid-samples are then tested, at any convenient place, by carefully pouring on to each about a half inch of a concentrated solution of ferrous sulphate, which need not necessarily be free from ferric sulphate. By looking at the colours produced thereby, in their succession from chamber to chamber, by comparing the drips and bottom-acids, looking at the strengths marked below, and taking into account the colour of the chamber-gas observed through the windows, a tolerably good idea of the process going on in the chambers is obtained. This certainly should be completed by an estimation of the sulphurous acid in the burner-gas and of oxygen in the escape-gas, and also by testing the nitrous vitriol &c., as we shall see in the next Chapter.

Kolb (Bull. Soc. Mulh. 1872, p. 309) gives a few analyses of chamber-acids confirming what has just been said.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Density	1·489	1·417	1·445	1·480	1·488	1·478	1·420	1·457
SO_4H_2	59·1	51·6	54·9	58·1	58·6	58·2	51·4	56·0
N_2O_3	0·023	...	0·04	0·023	0·010	0·02	0·170	0·03
N_2O_5	0·000	...	0·02	0·000	0·000	trace	0·040	0·00
SO_2...............	...	0·008						

a, acid from the first or denitrating tambour, where the sulphurous acid of the burner-gas meets the acid of the last chamber and the Guy-Lussac tower; *b*, the same when the chambers were short of nitre; *c*, acid from the tambour where the fresh nitric acid ran over the "cascade" (excess of nitre); *d*, the same, short of nitre; *e*, acid of the "large chamber;" *f*, acid of the last chamber, normal process; *g*, the same, large excess of nitric acid—liquid green and nitrous; *h*, the same, normal process.

The following rules may be laid down for the reactions which the various samples of acid from the chambers and drips ough to show. Generally speaking, all drips ought to show more nitre than the corresponding chamber-acids. The former represent the process going on in the atmosphere of the chamber, whilst the latter should act upon the nitre by their greater dilution, and actually do so. The *bottom-acid* of the *first chamber* ought not to show any nitre whatever; if it does so, it is a strong indication that the supply may be shortened. But first it must be ascertained if, on the other hand, the drip of this chamber does not show any nitre; for in this case it is proved that there is *too little steam* in the chamber, and that consequently the nitrous acid has been absorbed by the chamber-acid. Mostly this will be confirmed by both drip and bottom-acid being too strong; and then *more steam* must be given. If, however, *both* samples from the first chamber show nitre, some of the latter must be cut off, unless the supply has just been increased because the last chambers did not show enough; in this case the supply of nitre cannot be cut down till the last chambers have quite recovered.

Sometimes the first chamber-acid smells, on the contrary, of sulphurous acid: if this is the case to any appreciable extent, nitre is wanting.

The *middle* chambers ought to show already a faint reaction of nitre in the bottom acid, and a stronger one in the drips; the *last*, in any case, a moderately strong reaction in the bottom-acid and a very strong one in the drips. In this case also a deviation from the rule may proceed from various causes. For instance, the last chamber may be pale, and yet its bottom-acid may give a strong nitre-reaction. This may happen both if there is too much and if there is too little steam in this chamber: if the bottom-acid is too strong owing to the want of steam, it will dissolve too much nitre; if, however, there is too much steam present, that phenomenon will take place which, in chambers working without an absorbing-tower, is purposely caused: nitric acid will be formed, and will dissolve in the bottom acid. Both faults are easily avoided if the last chamber is not kept weaker than 90° nor stronger than 110° Tw.; but sometimes insufficient draught may cause that fault as well. If, on the contrary, the last chamber still appears red, and even the drips still show nitre, but the bottom-acid none, this is an indication which must be instantly met by increasing the supply of nitre; otherwise the chamber itself will soon become pale. If both indications coincide, a pale chamber and a ceasing or weakening of the nitre in the drip, this might still come from an excess of steam; but rarely will it be so, as anyhow that chamber does not get much steam. Three other explanations offer themselves—too little draught, too much draught, or too little nitre. Whether the draught is insufficient is most easily tested by estimating the oxygen in the escape-gas; whether it is too large, by estimating the sulphurous acid in the burner-gas; but in the case of very leaky chambers, which properly ought to have been stopped already, air enters directly into them, as is proved by the oxygen coming out too high in the escape-gas. Where no gas-analyses are made, the formerly mentioned external indications for judging of the draught are taken into account; but these are far more deceptive than gas-analyses. When the draught is not large enough, the nitric oxide does not meet enough oxygen to be oxidized; it is colourless, and, owing to its insolubility in strong vitriol, is altogether lost. This will be recognized by the appearance of red vapours on the gas issuing out of the chimney, where the nitric oxide is oxidized by the atmospheric oxygen, whilst the chambers themselves, where oxygen is missing, become pale. When there is too much air present, the nitrogen acids are carried away mechanically, and the chambers equally lose their colour; at the same time sulphurous acid goes away, as it has not time to be oxidized.

Insufficient formation of sulphuric acid in the chambers, from other causes, such as want of nitre or entering of air through chinks in the chambers and mechanical carrying-away of gas, will frequently *react upon the burners,* since by the insufficient condensation of gas the draught from the burners towards the chambers is diminished. Then all the appearances will take place which are caused by very bad draught in the burners, especially incomplete burning and formation of scars, which, again, weakens the draught. In this case as much nitre as possible must be given, in order to force a better formation of sulphuric acid; and, if necessary, even the burner-charges must be diminished.

But if the last chamber becomes pale, the draught being in order, and if its acid shows little nitre, it is just the want of the latter, and more of it must be introduced till the normal state has been restored. This will be confirmed by *testing the nitrous vitriol*, which will no doubt show a diminution of its nitre. To be sure, often several circumstances act at the same time, and make the process a complicated one. If, for instance, there is too little draught, so that, in lieu of N_2O_3 and N_2O_4, only NO or even SO_2 get into the absorbing-tower, not only will the draught have to be increased, but more nitre will have to be given as well, in order to make up for the loss. Just in the same way, when the nitre-gas has been mechanically carried away by an excess of draught (in which case, owing to its dilution, the Gay-Lussac tower cannot entirely retain it), not only will the draught have to be moderated, but more nitre will have to be introduced till every thing is in order again.

We thus see that, in nearly every case, when any thing goes wrong in the acid-chambers, an increased supply of nitre is at least temporarily necessary in order to restore the equilibrium, although the other two regulators, steam and draught, must always be taken into account at the same time; it is therefore very important that the possibility be afforded of temporarily introducing much more nitre into the chambers than is necessary in ordinary work; and every factory ought to possess facilities for it. If this should not be the case to a sufficient extent, and if without danger to the chambers it is not possible to introduce as much nitre as the case calls for, then nothing remains but to diminish the burning of brimstone or pyrites for a time, and to allow the chambers to recover their normal state by easing them in this way.

At some works the indications offered by the colour of the chambers and the reactions of the acids on nitre are not thought sufficient; but constant analyses are made to ascertain whether a definite and sufficient quantity of nitre is present in the apparatus. For instance, one manufacturer assumes 5 parts of nitric acid of 66° Tw. to be such, = about 4 parts of nitrate of soda to each 100 parts of pyrites burnt; as soon as the nitre contained in the Gay-Lussac and Glover towers and the chambers falls below this point, the supply of nitre is increased, and conversely. This appears very rational, but is very rarely done, perhaps partly because such estimations, in order to be at all accurate, require much trouble and take much time; nor is it possible easily to take into account the large quantity of nitre which exists in the atmosphere of the chamber.

The *temperature* of the acid-chambers is, by many manufacturers, observed with great care, as they believe that a regular and good chamber-process depends principally upon keeping the temperature always at a certain height, different in different parts of the apparatus. These manufacturers think that the formation of sulphuric acid only takes place regularly and completely within certain definite narrow limits of temperature. But it would appear as if here the cause were confounded with the effect; this is proved by the fact that the French and English manufacturers, who mostly work without a thermometer, obtain as good results as the German ones. It is indisputable that, *under equal circumstances* (that is, if the same set of chambers is served by the same number of burners, and if the chambers are protected from the weather by a building), the oscillations in the temperature of the chambers will not be very considerable. The sources of heat are always present—the heat of the burner-gas, that of the steam, and that given off by the chemical reaction itself. The latter is rendered evident by the fact that it is possible to raise the temperature of the chambers by increasing the supply of nitre. This is counterbalanced by the radiation from the thin and quickly-conducting walls of the chamber, by the heat contained in the escaping gas and in the bottom-acid drawn off. The radiation through the chamber-walls will vary very much according to the season, but not very much in the same season if the chambers are housed in. All causes leading to a faulty process—too much or too little draught, too much or too little steam, too little nitre—act, either directly by the heat of the gas itself or the steam, or indirectly by the disturbance of the chemical processes, on the temperature of the chambers; and thus it can be said that, for a given set and at the same outside temperature, the heat of the chambers ought only to show such oscillations as are inevitable by the successive changes in the burner-gas when new charges are made, and by the different energy of the acid-forming process in different parts of the chamber.

The oscillations in the same place by the intermittently larger or smaller quantity of the burner-gas and by the supply of fresh nitre, where there is no feeding with nitric acid, will vary according to the size of the chambers, but generally will not rise more than 3° or 4° C. Much more considerable are the differences found between various parts of the apparatus at the same moment. According to most observers, in the same chamber the region near the top is always warmer than that near the bottom, because the hotter and lighter gas naturally rises towards the former; the contradictory assertions of H. A. Smith have not been confirmed from any quarter within the author's knowledge. Further, the temperature of each chamber diminishes from front to back, and naturally even more that of the last chambers compared with the first. All these differences in the normal process ought to be constant. The first chamber will be generally so hot that one cannot touch it for any length of time, say 50° to 65° C.: in the absence of any cooling-apparatus, Glover tower, &c., the heat becomes so high that the lead cannot be touched with impunity; but in that case the chamber will not last very long. The second chamber mostly shows on the outside hardly more than blood-heat; thermometers with their mercury-vessels inside the chambers show from 40° to 60° C. The third chamber, if it be the last, will outwardly show little or no difference in temperature from the surrounding atmosphere; inside its temperature varies from 40° to 30°, and below that.

At the Aussig works in September the tambour showed 60°, the large chamber in its first part 45°, in its last part 43°; the first back chamber 30°, the last (kept without any steam) 20° C. At Oker the fore chambers in winter vary from 60° to 69°, the large chamber in its first part from 25° to 31°, in its last part from 19° to 25°; the back chambers 0° to 10° C. In summer the average temperature is 12½° C. higher than in winter.

The question now arises, Which is the best *absolute* temperature for the chamber-process in any given place of the apparatus? This, however, cannot be answered definitely, because the statements on this point vary too much, even if only the published ones are taken into account, and still more if private factory observations are regarded, letting alone the opinions of H. A. Smith differing completely from all others. No doubt some temperature must be the best for acid-making; but which this is, has not yet been experimentally decided; nor is it known to what extent the yield and the consumption of nitre are influenced by any deviations from the normal temperature up or down. Usually 45° to 50° C. is considered to be the normal temperature of the acid-chambers.

There is a pretty general agreement upon the point that in any case 60° C. is the highest temperature allowable for chambers, but that 50° or even less is preferable; this is also confirmed by Favre

(Monit. Scient. 1876, p. 272), according to whom, in the south of France at 65° C. the chamber-process is already disturbed. Little weight can accordingly be given to Payen's statement ('Précis,' p. 321) that the normal temperature is 55° to 60°, variable in winter between 50° and 70°, in summer between 65° and 80°.

The *lower* limit of temperature is by Schwarzenberg put at 40° to 50° C., because otherwise there would not be a sufficient quantity of water remaining in the state of vapour; he asserts that in cool weather a set of chambers is less easily started than in warm weather, and that in winter more nitre is used than in summer. The author must contradict this assertion of Schwarzenberg's, both from his own and from many other practical men's experience. Unless the temperature of the chambers sinks so low that ice is formed in them (which may happen with back chambers kept without steam), no excess of nitre is required in winter; on the contrary, at all well managed factories known to the author it is asserted that they regularly require less nitre in winter than in summer, and that the work altogether proceeds better in the cooler season.

It would not appear that the influence of temperature is so considerable as is usually assumed; for different works, employing similar raw materials, apparatus, &c., work at very different temperatures, without this being shown very clearly in their yield and consumption of nitre. Even the best English acid-manufacturers generally work without thermometers and in the open air, exposed to very rapid changes of temperature; yet, if otherwise well managed, their results equal those of the best continental works.

It is very well known to all practical men that the *depth of acid* at the bottom of the chamber influences the completeness and regularity of the chamber-process. The best yield and the most regular work is only obtained by keeping a good stock of acid in the chambers; but the author has not found that more than 9 inches depth makes any difference in this respect. Although a great depth of acid somewhat lessens the chamber-space remaining for the gas, the above fact is well established; but a satisfactory explanation of it has not yet been given.

By the observations and checks recommended in this Chapter it is possible constantly to know how the process is going on, and to keep it right. Any disturbances in the process can thus be removed, but less easily the longer they have continued. In the worst cases the work has to be interrupted altogether and started afresh.

In checking the process it must never be overlooked that the same symptom may be owing to various causes. Thus the acid may get weaker either by a falling-off in the make or by too much steam. The draught may be lowered either by a smaller make, or by atmospheric influences, or by the gas-flues getting stopped up with deposit. An insufficient conversion of sulphurous into sulphuric acid may be caused by too weak or by too strong a draught. The nitre may decrease in the chamber both from an excess of steam, which leads to formation of nitric acid, and from a deficiency of it, leading to chamber-crystals getting dissolved in the bottom-acid; and in both cases the strength of the vitriol falls off. Just because in acid-making a certain effect may be caused by different circumstances, the management of chambers is not an easy task, but requires a good deal of judgment and experience.

The most certain check on the process ultimately is always the *yield of acid and the consumption of nitre,* both of which should be ascertained once a week. We shall go into this in a later chapter. Mactear considers this check insufficient, and substitutes for it a direct estimation of the loss of sulphur in the escaping gas (Chem. News, xxxvi. p. 49). His way of calculating is a very roundabout one and little reliable, owing to the large amount of the possible sources of error. Still such a control of the process as is proposed by him is desirable; and it can be attained by continually aspirating a small quantity of the escape-gas, and, after absorbing the sulphur-acids, measuring it by a gas-meter or even by a large graduated aspirator. It seems the simplest plan to aspirate the gas through caustic-soda solution, adding a solution of potassium permanganate till a pink colour is just produced, and estimating the sulphuric acid then present (whether originally so or formed from sodium sulphate by oxidation) in the usual manner. The sulphur found can be calculated upon the total sulphur burnt from the oxygen of the exit-gas, preferably taken from an average sample of the whole day (compare above). The following formula may be used :—

$$(20{\cdot}95-a)\times 0{\cdot}009637\times\frac{1}{1{\cdot}00367}t\times\frac{h}{760}=x.$$

In this a denotes the percentage of oxygen in the exit-gas, t its temperature, h the barometrical pressure in millimetres, x the total quantity of the sulphur actually burnt, expressed in grams per litre of the exit-gas; with this the quantity actually found should be compared, in order to find the percentage of loss. The correction for barometrical pressure in most places may be omitted as unnecessary; that for temperature can be taken from the usual tables. It should not be overlooked that in this way no account is taken of the sulphur remaining in the cinders.

In a similar manner the escaping nitre-gas can be estimated; but this is much more difficult, since there is so very little of it, and nitric oxide is not easily absorbed. Potassium permanganate and hydrogen peroxide have been proposed for this purpose.

CHAPTER X.

THE RECOVERY OF THE NITROGEN COMPOUNDS.

The recovery of the nitrogen compounds which are still present in the gaseous mixture, consisting of nitrogen with a little oxygen issuing from the last chamber, has been previously mentioned as a process indispensable for the rational manufacture of sulphuric acid. It saves not merely two thirds of the nitre, but also a great deal (a quarter up to a third) of the chamber-space; it increases the yield of vitriol, and moreover prevents the escape of acid fumes into the atmosphere. Several processes may be employed for this object; but, with one exception, they only deserve a short mention. The only plan which has turned out successful in manufacturing practice, and which, certainly after a remarkable length of time, has been introduced into all well-managed works, is that which was proposed by Gay-Lussac as early as 1827, viz. the *absorption of the nitrous fumes by strong vitriol.* Only in Gay-Lussac's own country has his invention not yet been sufficiently appreciated; for in the south of France the recovery of the nitrous acid seems to be exceptional, if the report of Favre may be believed ('Moniteur Scientifique,' 1876, p. 223); Favre, himself manager of a factory in that neighbourhood, expresses himself as if the gas were regularly sent out of the last chamber direct into the atmosphere. Anyhow this still takes place at a large number of French works.

We must now first examine *the behaviour of sulphuric acid towards the oxides of nitrogen.* A great many chemists, some of them of first rank, have worked in this field; but the matter was first completely elucidated by the labours of R. Weber during the years 1862 to 1867. These form the basis of our present knowledge of this matter; they were published partly in the 'Journ. f. prakt. Chem.' lxxxv. p. 423 and c. p. 37, partly in Poggendorff's 'Annalen,' cxxiii. p. 341, cxxvii. p. 543, cxxx. p. 277, and partly in Dingler's 'Polyt. Journal,' clxvii. p. 453. Other very important papers have been published by Cl. A. Winkler ('Researches on the Chemical Processes going on in the Gay-Lussac Towers,' Freiberg, 1867), by Rammelsberg (Ber. d. deutsch. chem. Gesellsch. 1872, p. 310), by Michaelis and Schumann (ib. 1874, p. 1075). The latter introduced the scientific name "nitrosulphonic acid" for that compound which will chiefly occupy our attention, and which was previously known by the name of "chamber-crystals;" it is also known as "nitrosyl sulphate." The older researches of Clément-Desormes, Dalton, Davy, Berzelius, Gay-Lussac, W. Henry, Gaultier de Claubry, De la Provostaye, A. Rose, Koene, Weltzien, Rebling, and Müller have now merely an historical interest.

When we consider the different oxides of nitrogen, we can state for certain, in the first place, that *nitrous oxide*, N_2O, is no more soluble in sulphuric acid than nitrogen itself. Therefore all the nitre which in the chambers has been converted into nitrous oxide will be altogether lost.

Nitric oxide, NO, was said by Henry and Plisson to be absorbed by oil of vitriol, if left a long time in contact with it, with formation of nitrous pyrosulphuric anhydride (see below); but Berzelius, Gay-Lussac, and many others have already refuted this statement, more especially Winkler (*l. c.* pp. 5 to 8). This proves that the sulphuric acid of the absorbing-apparatus cannot retain that portion of the nitrogen oxides which has been reduced to the state of nitric oxide; and from this follows the necessity of an excess of oxygen in the gas issuing from the chambers, since only this prevents the existence of nitric oxide in the same. Traces of nitric oxide may, however, escape oxidation even in the presence of oxygen.

In the presence of oxygen nitric oxide is absorbed by sulphuric acid (Bussy, Winkler); but then it is really nitrous acid which is absorbed; and Winkler has proved that it is precisely the presence of sulphuric acid which causes the oxidation not to proceed beyond the formation of nitrous acid, the latter combining afterwards with the sulphuric acid to form nitrosulphonic acid and water:—

$$2SO_2(OH)_2 + N_2O_3 = 2SO_2(OH)(NO_2) + H_2O.$$

Nitrous acid (of which only the anhydride, N_2O_3, has been obtained in the free state; the hydrate, NO.OH, is only hypothetical) as well as *hyponitric acid* or *nitrogen tetroxide*, NO_2 or N_2O_4, dissolve in sulphuric acid, so long as the latter has not been diluted beyond a certain degree, and thereby form the compound $SO_2(OH)(NO_2)$, already designated as *nitrosulphonic acid**, according to the equations

$$\text{I. } 2SO_2(OH)_2+N_2O_3=2SO_2(OH)(NO_2)+H_2O, \text{ and}$$
$$\text{II. } SO_2(OH)_2+N_2O_4=SO_2(OH)(NO_2)+NO_2.OH;$$

that is to say, in the case of nitrous acid merely with splitting off of water—in the case of hyponitric acid, however, with the simultaneous formation of nitric acid, which likewise remains dissolved in the sulphuric acid. According to Rammelsberg (*l. c.*), however, in the case of nitrous acid being employed in excess, the following reaction may also take place—

$$\text{III. } SO_2(OH)_2+2N_2O_3=SO_2(OH)(NO_2)+NO_2.OH+2NO;$$

that is to say, besides nitrosulphonic acid, nitric acid and nitric oxide are also formed.

Nitrosulphonic acid is obtained as a crystallized mass by the union of nitrous anhydride with oil of vitriol (Weltzien), but as a solution in sulphuric acid in the presence of not too much water; such a solution also remains behind on heating a mixture of oil of vitriol with concentrated nitric acid (A. Rose). It is also formed from sulphuric anhydride and the oxides of nitrogen in the presence of water (Doebereiner, Gaultier de Claubry, Kuhlmann). Of much greater importance is its formation from *sulphur dioxide* and the oxides of nitrogen in the presence of water, or of water and oxygen. In the absence of water, sulphur dioxide, whether in the gaseous or the liquid state (at —20° C.), acts neither on nitric oxide nor on the hyponitric acid formed therefrom by access of air; but a small quantity of water causes the formation of crystals of nitrosulphonic acid (Davy, Gaultier de Claubry, Winkler): it cannot be otherwise, as the constitution of that compound requires hydroxyl. This is precisely the way in which the chamber-crystals are formed in the lead chambers.

Winkler has proved (*l. c.* p. 14) that even in the presence of moisture sulphur dioxide does not form chamber-crystals with pure

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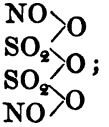
* According to Cl. Winkler (see below), nitrogen tetroxide dissolves in sulphuric acid of 170° Tw. *as such*, without any change.

N_2O_3, but NO is formed in that case. Also from NO_2 and SO_2, if they are *quite dry*, no chamber-crystals are formed; but they appear at once if only a drop of water is added. Winkler makes use of this behaviour in order to distinguish nitrous from hyponitric acid, since the former in an atmosphere of carbon dioxide does not form chamber-crystals with sulphur dioxide, even in the presence of moisture, but the latter does so.

It is no contradiction to this, that the crystals are obtained from dry SO_2 and NO_2 in the presence of a little oil of vitriol (Weber), or from SO_2 and nitric acid NO_3H (Sestini). The experiments of H. A. Smith (in Bode's translation of his pamphlet, p. 27) were to prove the contrary, viz. that dry sulphur dioxide and "nitrous gas" show a reaction even in a *perfectly dry* vessel, but "much more quickly on the introduction of a drop of water" (according to his description, the "dry nitrous gas" is made from sulphuric acid and nitrate of soda, and therefore contains at least nitric hydrate NO_3H); but the crystals formed thereby he considers to be not ordinary chamber-crystals, but sulphuric anhydride (!), since they are acicular (Smith evidently has never seen the splendid acicular groups of chamber-crystals which are so easily formed as a lecture experiment)—further, since they remain a pretty long time unchanged (this is just the behaviour of chamber-crystals in air containing not too much moisture, whilst sulphuric anhydride is much more deliquescent), and since they dissolve in contact with water without an effervescence of nitrous gas (this, according to Frémy's and the author's own observations, happens with nitrosulphonic acid if a large excess of water is present). A special refutation of his extremely crude experiments is all the less necessary as he has not adduced a shadow of a scientifically valid proof for his assertions which differ from those of all other chemists.

According to Winkler, therefore (*l. c.* p. 15), fumes of ***nitrous acid*** with an excess of sulphurous acid and water, and with exclusion of oxygen, give no chamber-crystals at all; but they are decolorized, nitric oxide and sulphuric acid being formed. If oxygen or air are admitted, chamber-crystals instantly appear, and also if ***hyponitric acid*** in the presence of water meets sulphurous acid. This agrees with the results of all other chemists.

There exists also a similar compound, which contains no hydrogen, the ***nitrous pyrosulphuric anhydride***, N_2O_3, $2SO_3=$



$$\begin{array}{ll}\mathrm{NO} & \\ & >\mathrm{O} \\ \mathrm{SO_2} & \\ & >\mathrm{O}\,; \\ \mathrm{SO_2} & \\ & >\mathrm{O} \\ \mathrm{NO} & \end{array}$$

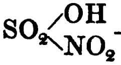
but this is only formed by mixing liquid sulphur dioxide and nitrogen tetroxide in the cold under pressure (Provostaye), or sulphuric anhydride with dry nitric oxide (H. Rose), or by heating sulphuric anhydride with nitrogen tetroxide (Weber), none of which reactions are possible in the manufacture of sulphuric acid.

Neither is this the case with the compound produced by R. Weber (Poggend. Annalen, clxii. p. 602) by conducting sulphuric anhydride into the most highly concentrated nitric acid, which has the empirical formula N_2O_5, $4SO_3$, $3H_2O$.

The easiest way of preparing the chamber-crystals in a state of purity is, according to Weber, by conducting sulphur dioxide into well-cooled fuming nitric acid until the whole mass has been converted into a magma, but not until the nitric acid has been entirely decomposed, and drying the crystallized mass on a brick under a bell-jar alongside some oil of vitriol. Obtained in this way, or collected in the connecting-pipes of vitriol-chambers or other places where there is a deficiency of steam, they consist of four-sided prisms or orthorhombic crystals; but generally, when prepared on the small scale, they appear as a scaly, feather-like, or granular mass, colourless and transparent. Their fusing-point is stated by Weltzien=73°, by Gaultier de Claubry=120° to 130°; but they are partly decomposed before fusing, with evolution of red fumes.

The composition of chamber-crystals was formerly uncertain; the question was, in the language of the older chemists, whether they were a compound of sulphuric acid with hyponitric, or with nitrous acid. Müller (Ann. Chem. Pharm. cxxii. p. 1) still pronounced for the former; but R. Weber proved in 1862, and more rigorously in the following year, by estimating all their constituents according to unexceptionable methods, that their formula must be constructed on the second supposition. His results were as follows:—

	Molecular weight.	Calculated.	Found.
$2SO_3$	160	62·99	64·00
N_2O_3	76	29·92	27·96
H_2O	18	7·09	10·50
$2SO_3$, N_2O_3, H_2O	254	100·00	102·46

This formula has also been confirmed by Michaelis and Schumann (*l. c.*), who at the same time proved, from the products of decomposition by phosphorus perchloride, that the compound whose molecular weight has to be halved must be regarded as *nitrosulphonic acid*,  $SO_2\langle^{OH}_{NO_2}$—that is, as sulphuric acid, one of whose hydroxyls is replaced by the nitro group, or as nitric acid for whose hydroxyl is substituted the sulpho group.

The chamber-crystals are not changed by a little water, if they absorb it from moist air and deliquesce in the same after some time; but in liquid water they dissolve quickly with evolution of heat and nitric oxide, to form dilute sulphuric acid, from which much more nitric oxide is given off on boiling. When introduced into a large quantity of water, they dissolve without evolution of gas (Frémy). Many contradictory explanations have been given of the reactions going on therewith, for instance by W. Henry, A. Rose, Thomson, &c.; but a few experiments made by Philipp according to the directions of Rammelsberg (*l. c.*) have alone cleared up the matter. It has been proved that on dissolving chamber-crystals in water a quarter of their percentage of nitrogen escapes as NO; the remainder of the nitrogen remains dissolved along with the sulphuric acid, partly as nitrous, partly as nitric acid; in the cold the proportion is 20 of the latter to 80 of the former. Most probably, of the 11 per cent. of nitrogen contained in chamber-crystals on dissolving them in water, ¼ appears as nitric oxide, ⅝ as nitrous acid, and ⅛ as nitric acid. Whilst, therefore, the usual statement of the reaction between chamber-crystals and water is this,

$$2SO_2(OH)(NO_2) + H_2O = 2SO_2(OH)_2 + N_2O_3,$$

Rammelsberg's results lead to the following equation:—

$$\begin{aligned}16SO_2(OH)(NO_2) + 9H_2O = 16SO_2(OH)_2 + 4NO \\ + 2NO_2(OH) + 5N_2O_3.\end{aligned}$$

The first, simpler, equation, however, will in most cases suffice to represent of the reactions within the chambers.

The behaviour of nitrosulphonic acid towards sulphuric acid is of even more immediate interest for us. In concentrated oil of vitriol the crystals dissolve easily and without decomposition; this solution is stable enough to be distilled without losing any nitrous acid, whilst the isolated crystals are decomposed on being gently heated.

If the above solution be half distilled, the residue will be richer in nitrous acid. It is possible to obtain solutions of 1·9 sp. gr.: they evolve with water nitric oxide, inflame phosphorus at 62° C., oxidize sulphur and many metals on distillation with evolution of NO; heated with ammonium sulphate to 160° they evolve nitrogen gas. This solution of nitrosulphonic acid in strong oil of vitriol (of 170° Tw.), even on long-continued treatment with dry sulphur dioxide, is only incompletely decomposed, and on addition of water still shows the presence of nitrous acid by the evolution of brown vapours. This explains the fact (well known to manufacturers) that *concentrated* vitriol contaminated by nitrous acid is only with difficulty purified by sulphurous acid. Heated, sulphurous acid decomposes chamber-crystals with evolution of nitrous oxide (Frémy). Further statements on the behaviour of sulphurous acid towards the solution of chamber-crystals in sulphuric acid, the so-called "nitrous vitriol," will be made when examining the process going on within the Glover tower. It is remarkable, and of great importance for the practice of sulphuric-acid-making, that even dilute acids of 1·70 down to 1·55 sp. gr. dissolve the crystals in the cold without decomposition; the decomposition only commences when the specific gravity of the dilute acid has fallen below 1·55 —that is, below the density of ordinary chamber-acid (Weber). Such dilute solutions are formed when hyponitric acid meets dilute sulphuric acid, according to equation II. on page 366; and just this always happens in the chamber-process. If, according to Weber, hyponitric acid, made by gently heating fuming nitric acid (and therefore in any case not free from nitric acid), be added to sulphuric acid of different degrees of concentration, the following is observed:—The strongest oil of vitriol, down to 1·7 sp. gr., absorbs the hyponitric acid without coloration. Acid of 1·55 turns yellow: here the hyponitric acid is probably absorbed to a large extent similarly as by nitric acid, and no decomposition, as represented by equation II. on page 366, has taken place, whilst this has to be assumed in the case of the stronger acids. Acid of 1·49 turns greenish yellow, of 1·41 intensely green; acid of 1·31 turns blue and evolves nitric oxide, which on applying a gentle heat escapes with violent effervescence. (It is most probable that the decomposition here takes place according to the equation which Rammelsberg has established for the decomposition of chamber-crystals with water, see p. 369.) Weak acids are only coloured for a short time. From this may be inferred:—that acids of 1·8 to 1·7 combine with hyponitric acid with formation of nitrosulphonic acid; weaker acids simply absorb it; and the more dilute acids decompose it with formation of nitric oxide, nitrous acid, and (according to Rammelsberg) nitric acid. The action of sulphurous acid on these mixtures is different according to their concentration. As mentioned above, the solution of chamber-crystals in concentrated vitriol is but incompletely decomposed even by a prolonged action of sulphurous acid; but the yellow mixture of 1·55 sp. gr. and the coloured more dilute acids are decomposed with strong effervescence of nitric oxide. It will soon be shown what part all these reactions play in the recovery of the nitrous gas in the manufacture, where the object is first to absorb the gas sulphuric acid of 1·7, and then again to liberate it from that solution.

Winkler gives a different account of the behaviour of liquid hyponitric acid from that of Weber. He states that it may be mixed with sulphuric acids down to 142° Tw., but that it yields a solution totally different from that of chamber-crystals in sulphuric acid, viz. one of a yellow colour and constantly evolving red fumes. On heating, it effervesces and gives off streams of gaseous hyponitric acid; if the mixture was made with sulphuric acid of 142° Tw., the NO_2 completely volatilizes far below the boiling-point of sulphuric acid, so that the residue on dilution with water does not decolorize potassium permanganate. If, however, acid of 170° Tw. has been employed, the liquid on heating certainly yields up the larger portion of its NO_2; but the residue behaves like a solution of chamber-crystals in sulphuric acid, and on being mixed with water it evolves red fumes which can be proved to be N_2O_3, not NO_2, by their not forming any chamber-crystals with moist SO_2.

There are some essential differences between the statements of Weber and those of Winkler, more especially as far as the behaviour of hyponitric acid is concerned, which must be cleared up by further researches.

If concentrated sulphuric acid is mixed with a little concentrated *nitric acid*, and sulphurous acid is passed into the mixture, the nitric acid in the cold is only reduced to nitrous acid, which remains combined with the sulphuric acid; this compound resists the further action of the sulphurous acid, similar to the solution prepared from concentrated oil of vitriol and chamber-crystals. On the other hand more dilute mixtures of sulphuric and nitric acid, below 1·7 sp. gr., are more or less easily decomposed by sulphurous acid, in the ratio of their dilution. We shall see that these observations of Weber's have also to be taken into account in explaining the process in the chambers and in the Glover tower.

From the above theoretical researches it follows that all oxides of nitrogen down to N_2O_3 are absorbed easily by sulphuric acid of 1·7 sp. gr. and upwards, less easily by weaker acid, not at all by acid of less than 1·5 sp. gr. But neither NO nor N_2O are absorbed by sulphuric acid. Thus sulphuric acid of moderate strength presents a means of taking from the gas escaping from the chambers its nitrogen acids (nitrous gas); a second process must then follow, by which the sulphuric acid charged with nitrous gas (commonly called "nitrous vitriol") is again deprived of its nitrogen compounds. Both processes have to be described consecutively.

By far the most usual *apparatus for retaining the nitrous fumes* by means of strong sulphuric acid is the coke-tower, first employed in 1827 by Gay-Lussac, and justly designated everywhere by the name of its inventor. From the facility which this apparatus gives of retaining at least two thirds of all the nitre, and from the other important advantages realized by it (see p. 364), it might have been expected that that apparatus would have been generally introduced within a short period after its invention. But, most curiously, Gay-Lussac's invention was only carried out into practice for the first time in 1842, at Chauny; and forty years after his invention the majority of sulphuric-acid makers did not possess either Gay-Lussac's or any other apparatus for retaining the nitrous fumes; nay, even some of those who had adopted it in the first instance had abandoned it again.

The cause of this was that at that time the only plan of denitration was by dilution, and that the expense of concentration, of pumping the acid, &c. was thought to amount to nearly as much as the saving of nitre. Most manufacturers were not aware that the saving (which was mostly estimated too low, viz. equal to one half of the nitre) was not the only advantage of the absorbing-towers. But the great dearth of nitrate of soda which occurred ten years ago brought the matter vividly before them; at the same time on the continent the composition of the chamber-gases, the chamber-space, &c. was studied more closely, and the advantage of an excess of nitrous gas in the chambers, which can only be secured by means of an absorbing-tower, became evident. These circumstances led to such towers being erected again, and the more so as some few manufacturers had never given them up at all and had done very well with them.

In England, where the theoretical part of the subject has been much less attended to, another practical invention had in the meantime been made, which entirely removed the only essential drawback of the Gay-Lussac absorbing-tower, viz. the necessity of concentrating the acid; this was the *Glover tower*. Whilst little more than ten years ago only a comparatively very small number of English works absorbed their nitre-gas at all, since then all the larger and better works have introduced the Gay-Lussac absorbing-column, nearly always along with Glover's denitrating column. Probably some few exceptions may still survive; but we are here only speaking of works somewhat rationally managed. Even in 1873 very few English works' chemists were as depreciatory in their judgment, and at the same time as ignorant of the essence of Gay-Lussac's apparatus, as H. A. Smith showed himself to be in his pamphlet (Bode's translation, p. 82). His assertion that the Gay-Lussac tower was an outcome of negligence, since with greater care no loss of nitrogen compounds at all need be suffered, proves him ignorant of the reason why an excess of those compounds is purposely employed, which must afterwards be reabsorbed, viz. that the sulphurous acid may be fully oxidized. Directly after, he speculates in what way the sulphurous acid escaping "in the majority of works" may be utilized—a question which in working with the absorbing-tower does not exist, as such escapes are then too insignificant. The necessary answer to Smith's reasoning has been already given by his translator very thoroughly (p. 121, note).

Gay-Lussac's Absorbing-Tower for Nitrous Gas

consists of a chamber, placed at the end of the set of lead chambers, higher than wide (a "tower" or "column"), of which the walls are made of a material capable of resisting sulphuric acid, and the interior space is filled with a material presenting a large surface. By means of this "packing" a stream of sulphuric acid entering the column from above is divided into small drops; at the same time the current of gas rising up in the tower is divided into many small jets; and thus the contact between the gas and the acid, covering the surface of the packing, is multiplied. The principle applied here is exactly the same that had been employed for a long time in the "scrubbers" of gas-works, in order to deprive the gas of ammoniacal salts by washing it with water, and which is also applied to the condensation of muriatic acid in the decomposition of common salt (Book II.). It is always this, to produce a great many points of contact between the gas and the absorbing agent, and thereby to wash out the absorbable substance of the gas as much as possible; or the interior of the tower may be represented as a filter which allows only the inert gas to pass, but retains the gas acted upon by the absorbing agent.

The reason why such an apparatus is constructed in the shape of a tower or column (that is, why it is made much higher than wide) is this, that in the case of apparatus with a considerable horizontal section it is quite impossible to distribute a comparatively thin stream of the absorbing liquid equally over the whole section, and at the same time to force the gas to meet the liquid. Of course, the gas has always a tendency to rise where its way is not barred wholly or in part by a liquid; unless the columns are pretty narrow, it is not possible to prevent the liquid running down almost entirely in some places, the gas rising in other places, so that but little of the two would come into contact, and the liquid would arrive at the bottom charged with very little absorbable matter, whilst the gas issuing at the top would still contain a good deal of it.

Hence follows this general principle:—An apparatus for the absorption of gas, such as are in question here, should be made no wider than is necessary in order that the draught may not be impeded by the packing; and the necessary cubical volume of the packing should be obtained by making the tower so much higher. Thereby another object is also attained: viz., the gas entering at the bottom of the tower, where it is richly charged with absorbable matter, meets a liquid containing already a good deal of the same, and therefore not capable of dissolving much more, unless an abundant supply is presented to it, which is just the case under these circumstances; on the other hand, the gas near the top of the tower, where it is almost entirely deprived of its absorbable parts, meets entirely fresh liquid, which is able to seize upon them even in a poor gas, whilst a partly saturated liquid would have no action upon such a gas. This is the theoretical explanation of the practical fact that a *saturated* absorbing liquid, along with *exhaustion* of the gas, can only be attained by building the towers very high.

A considerable vertical height of the absorbing medium can certainly be also obtained by placing two towers alongside of each other, and compelling the gas leaving the first tower at the top to pass downwards in order to rise again in the second tower. As a rule this arrangement is not to be recommended, for two reasons:—first, there is a loss of draught caused by compelling the gas to take the unnatural path downwards for a portion of its course, and the consequent great friction in the connecting-tube; secondly, in this way certainly the gas can be completely washed out, but at the same time there does not result a saturated absorbing liquid, both of the towers having to be fed with liquid, which at the end only attains *half* the degree of saturation that would have been attained in *one* tower equal in height to both those employed and fed with a single jet. Only, where the strength of the absorbing liquid is of no consequence, it is often more convenient to employ two towers one after the other than one of double the height. An arrangement still less recommendable is found in many books and in a few badly arranged works, where, from mistaken economy, the absorbing-tower is made of twice the usual horizontal section, and divided into two halves by a partition, in order to pass the gas up one half and down the other. The saving in cost as against two towers or a tower of double the height is not very considerable; on the other hand, that half of the tower in which the gas has to descend is almost entirely sacrificed, because here, where the gas and the liquid travel in the same direction and next to no friction takes place between them, their mutual action, as experience shows, is very inconsiderable; both mostly travel downwards peacefully without interference, and arrive at the bottom almost unchanged. The arrangement of a double tower is inadmissible unless the partition extends right through, and the gas issuing from the one division passes downwards by a special pipe, and is allowed to ascend again in the second division, and thus to *meet* the acid rain. This comes to the same thing as placing two towers alongside each other. Such an apparatus is but rarely met with for absorbing nitre-gas, a little more frequently as a condenser for muriatic acid. As we have treated of them here, in the Chapter treating of the latter subject the principle (which is exactly the same in both cases) will not need to be explained again.

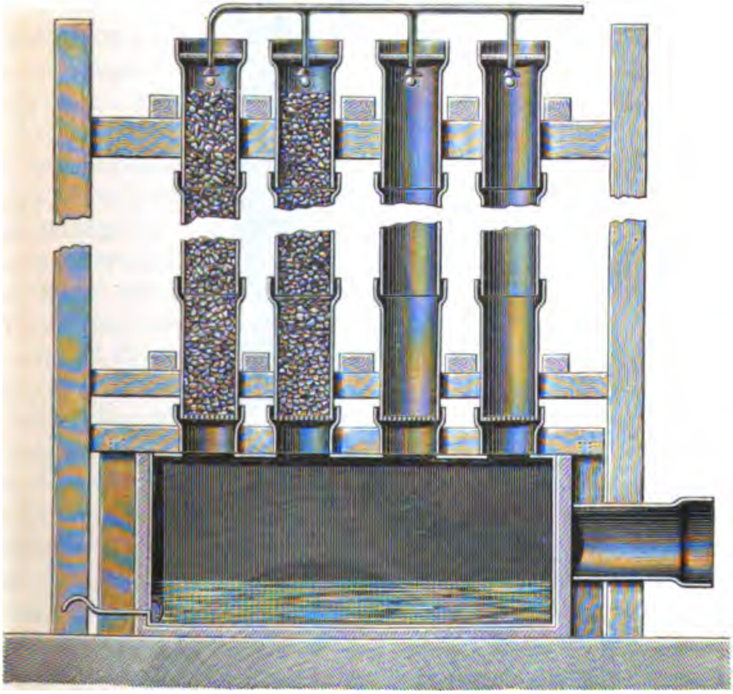
As far as the *width* of the absorbing column is concerned, it should be considerably wider than an empty tube of sufficient diameter for the current of gas, not merely because the packing of the tower occupies a large portion of its section and only leaves a small portion of it as clear space, but also because the packing must be purposely arranged so as to divide the current of gas into a great many separate jets, constantly changing their direction, and to expose them to the largest possible amount of *friction* at the surfaces of the packing wetted with the absorbing liquid. The tower must therefore be wide enough to take account of this purposely increased friction. Furthermore, it has to be considered that the *slower* the current of gas, the more time will be afforded for the action of the absorbing liquid, and the more perfect the latter will be. This would lead to giving the tower as wide a section as possible, in order to slacken the speed of the gaseous current. As, for the reasons stated above, this plan cannot be carried out very far, the inference is that a certain middle path is to be taken: a tower should be made wide enough not to hinder the draught, and to leave sufficient time for the contact of the gas and the liquid, but not so wide that the liquid cannot be spread equally all over and that the gas can go past it. Evidently no exact calculations can be made as to the proper width; only practical experience can decide; and this has shown that a Gay-Lussac tower should never exceed 7 feet in width, but that it is better made no more than 5 feet wide even in the case of large sets of chambers, and that, if a larger section is indispensable, a double tower should rather be constructed.

The dimensions of the absorbing column are necessarily correspondent to those of the set of chambers; its cubical contents should be at least 1 per cent. of the chamber-space. For sets of from 140,000 to 200,000 cubic feet the column ought to be 6 feet in width and 50 feet high; for a set of from 70,000 to 100,000 cubic feet a tower from 4 to 5 feet in width and 40 feet high is sufficient. In both cases it is best to give the tower an additional height of 10 feet; there will be all the more saving of absorbing acid the higher the tower and the longer the way for the acid. These statements refer to chambers working with pyrites; with brimstone the height of the tower need not exceed 26 feet.

In all probability a larger absorbing-space, say 2 per cent. of the chamber-space, would permit working with a larger economy of nitre than the above-stated sizes; in the case of large sets this space would then mostly have to be divided into two towers. In fact, the absorbing-space at the Jarrow chemical works has lately been raised to 90 cubic feet per ton of pyrites per week, which amounts to about 2 per cent. of the chamber-space; and by this the consumption of nitre has been brought down from 1·45 to 1·05 part per 100 parts of pyrites.

The *material* for constructing Gay-Lussac towers is generally lead, more rarely stoneware pipes, still more rarely stone flags. The cheapest plan would probably be to use 9-inch earthenware pipes, of which a larger number would be placed over a trough of stone or of wood lined with lead in the way shown in fig. 159, so that the gas would rise in all the pipes, whilst each pipe was fed by a small jet of acid by means of an oscillating bucket or an intermittent siphon. The pipes would have to be filled with coke; and

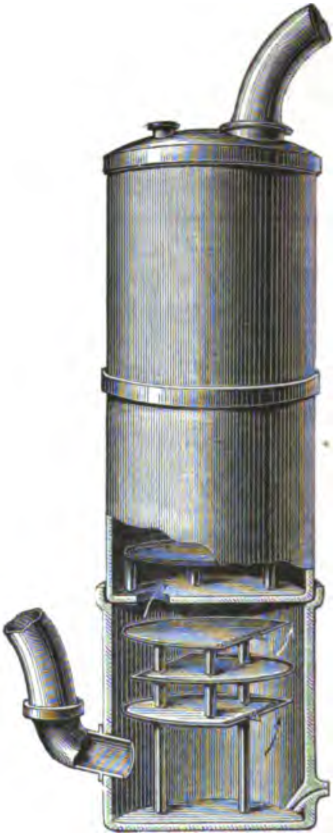
Fig. 159.



there would have to be a sufficient number of them to give the necessary horizontal section. The author does not, however, know of such an apparatus having been anywhere put into operation.

A stoneware apparatus manufactured by Fikentscher, of Zwickau, and represented in fig. 160, used in several works, is said to have given good results; but the surface of the acid in it must be much smaller than in a coke-tower.

Fig. 160.



In most cases the absorbing-tower is made of lead and packed with coke. The lead in continental works is often made unnecessarily thick, from 14 to 28 lb. to the square foot; in British works it is often no more than 7 lb. or even 6 lb. to the square foot, like the chamber-lead. There is no reason why the lead should be stronger: the gas, as well as the acid, in this apparatus are only moderately warm, and, indeed, ought to be as cool as possible; nor is the lateral pressure of the coke, if properly packed, so great that it need cause any fear. At any rate the lead sides are necessarily supported by a wooden frame. Both circular and square towers are found; the former take less lead for the same area. They are frequently lined inside with bricks, which are put in dry along with the packing; "split bricks" of 1 inch thickness are often employed for this purpose, lest too much space should be lost. The object of this lining is to prevent the coke from cutting the lead in settling down. It seems hardly worth while to go to the expense of the lining, and at the same time to lessen the area of the tower, for such a small matter, which can be easily remedied by putting on a patch of lead; the lateral pressure of the coke would only be avoided by making the lining 9 inches thick, which is rarely done, as it wastes too much space.

The *foundations* of the tower must, of course, be very substantial, and, if possible, constructed in such a way that any acid running over will not damage them. It is preferred to make them high enough to avoid the gas from the last chamber having to descend towards the tower; if, however, the chambers are very high above the ground, this would involve considerable difficulty and expense, and the tower is then raised only high enough above the ground to leave a natural fall from its bottom to an acid-tank, and from this to the pumping-apparatus for the nitrous vitriol.

The *packing* of the absorbing column, it has already been said, is nearly always *coke*. In a few places, instead of coke, broken bits of earthenware or of glass, or even pieces specially moulded for this purpose, are employed, or very thin tubes in regular layers, standing upright. The former have too little action; the latter are good, but too dear. Coke is therefore almost universally preferred: owing to its irregular shape and rough surface, its low price, and its long duration, it is both the cheapest and the best medium for dividing the acid into as small drops as possible, and thus offering to the gas the largest possible area of contact with the acid. Coke is also preferable to the other materials in question on account of its lightness. Sometimes it is stated that coke is esteemed useful for this purpose because of its porosity; but this is erroneous. In the first place, porous coke is worthless for a coke-tower, for which dense coke is indispensable; secondly, the pores would at once be filled with liquid, which thus would not come into contact with the gas passing outside. It is not owing to its porosity, but to its rougher, more irregular, and therefore much larger surface, that coke is preferable to broken glass or earthenware &c.

It is necessary to be very careful in the selection of the coke. Gas-coke is of no use at all here, only the hardest-burnt oven-coke, giving a clear ring and as little porous as possible, of a silvery white, not of a dull black. It must be carefully packed, and all dull black pieces rejected. First only the large pieces, a foot and upwards in length, are picked out; these are placed in horizontal layers directly over the grating of the tower, crossing each other if possible; each piece must be placed by hand, inconvenient as it is that the workman has to be lowered down from the top to the bottom of the tower, and must receive his material in the same manner. Thus the first third of the tower is packed; then come the pieces next in size; and for the last third the smaller lumps may be used, and may be simply emptied in out of baskets. Nothing, however, is allowed to go into the tower which has not been sifted on a riddle with three-inch holes. Unless a coke-tower is packed most carefully, either the draught through it will be impeded, or there will be too much way left for the gas, or, in the most frequent and worst case, the packing will be too loose in some places and too dense in others, and thus there will be bad absorption along with bad draught.

Soft porous coke has to be rejected for two reasons: first, it cannot support the pressure of the superjacent column without being crushed, thus stopping the draught; secondly, such soft coke is soon acted upon by nitrous vitriol (which has next to no action on hard coke), and is ultimately converted into a thick paste; this is very bad for the draught, and may necessitate repacking the tower.

The above general remarks must now be supplemented by the description of a few apparatus actually constructed. First, we shall give a description of the Freiberg coke-tower, from Schwarzenberg's 'Chemical Products,' pp. 384–390. Fig. 161 is a sectional elevation, fig. 162 a sectional plan of the apparatus used at Freiberg for the recovery of the nitrous compounds, on a scale of

Fig. 161.

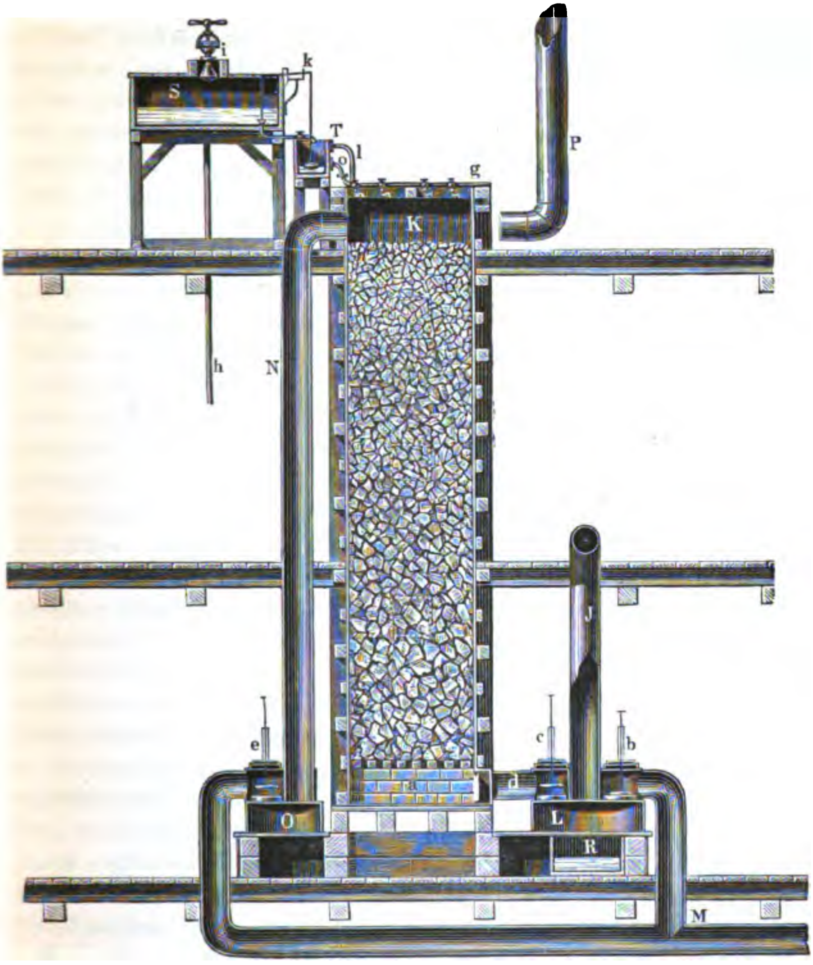
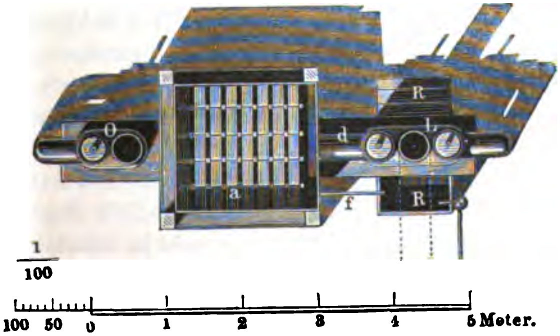


Fig. 162.



1 : 100. Its principal portion is the lead tower *k*, 5 feet 7 inches wide and 26 feet 3 inches high, supported by a timber frame similar to that of a lead acid-chamber. The cover, however, is not burnt to the sides, but can be taken off. It consists of a wooden frame, lined inside with lead, with a flange standing up all round the edge; the latter, when the cover is put on, fits into a channel worked into the side sheets, which are turned horizontally over the crown-tree; by filling this channel with sand a tight lute is produced. On the bottom of the chamber a kind of grating is constructed of hard-burnt fire-bricks, consisting of parallel walls, forming channels of about 1 foot 8 inches height. They are covered in such a way that between the covering-tiles empty spaces of about 2½ inches remain, through which the gas can freely pass from below and the acid from above. On this grating the coke is packed, with which the tower is filled close up to the exit-tube N, the larger pieces at the bottom and gradually smaller ones towards the top. In order to put these pieces in more conveniently, three man-holes are made in the side, consisting of wooden frames lined with lead and made tight with putty at the joints. From the last lead chamber the gas arrives in the tower through the pipe J, passing on its way the valve-box L, which allows it to be taken away direct through the tube, without any interruption of work, in special cases—for instance, repairing or repacking the tower. For this object the valve *b* is opened and *c* is shut. If, on the other hand, the valve *b* is shut and *c* is open, the gas first goes through the short pipe *d* into a small space projecting at the bottom of the tower along the whole of one of its sides; from this it divides itself among the channels below the grating, and then ascends through the coke; at the same time sulphuric acid of about 152° Tw. trickles down through the coke, absorbing the nitrous acid out of the gas, and carrying it down as a solution of "chamber-crystals" or "nitrous vitriol." The gas deprived of nitrous acid goes away through the pipes N and M, again passing a valve-box, O, which serves as a means for interrupting, by closing the valve *e*, the communication between the tower and the pipe M, if the gas is not to go through the tower, but direct into the pipe M.

The nitrous vitriol runs from the tower through a tube *f*, visible in the plan fig. 162, into a tank R, from which it goes into the "steam-column," in which its nitrous acid is driven off again for further use, as we shall see below.

At the Freiberg works the above-described tower is situated close to the steam-column, which stands beside the first lead chamber, into which the nitric acid is introduced. This arrangement causes the gas escaping from the last lead chamber to travel through a very long pipe to the tower. The friction in this pipe and the further checks caused through the ascending and descending of the gas are probably the reasons why, at Freiberg, it has been found necessary to connect the exit-tube M with an aspirating chimney. Schwarzenberg is against the use of a chimney, and prefers, therefore, to place the apparatus immediately beside the last lead chamber, so that a very short connecting-tube takes the gas from the latter into the tower, and a long lead tube the nitrous vitriol into the steam-column. In this case the aspiration of the gases through a chimney is unnecessary; they can be taken away direct into the atmosphere from the top of the tower through a pipe P, of which a piece can be seen in fig. 161. We have seen before that the employment of chimney-draught, which Schwarzenberg rejects, can be looked at in a very different way; and we have remarked that the draught in this case can be regulated with great ease, and the "sight" can be very conveniently placed. Large sets of chambers, indeed, almost regularly work with a chimney, and do better than small sets without the same. Instead of the loose cover and fixed bottom of the Freiberg towers, most works prefer a fixed cover with a man-hole hydraulically luted and an independent bottom with upstanding sides, similar to a chamber-bottom. Instead of the grating made of fire-bricks, many works have a kind of dry arch (see below). In a few cases iron rods covered with lead are used; but these cannot be recommended, as the lead may be cut in some places, and the iron would then be acted upon.

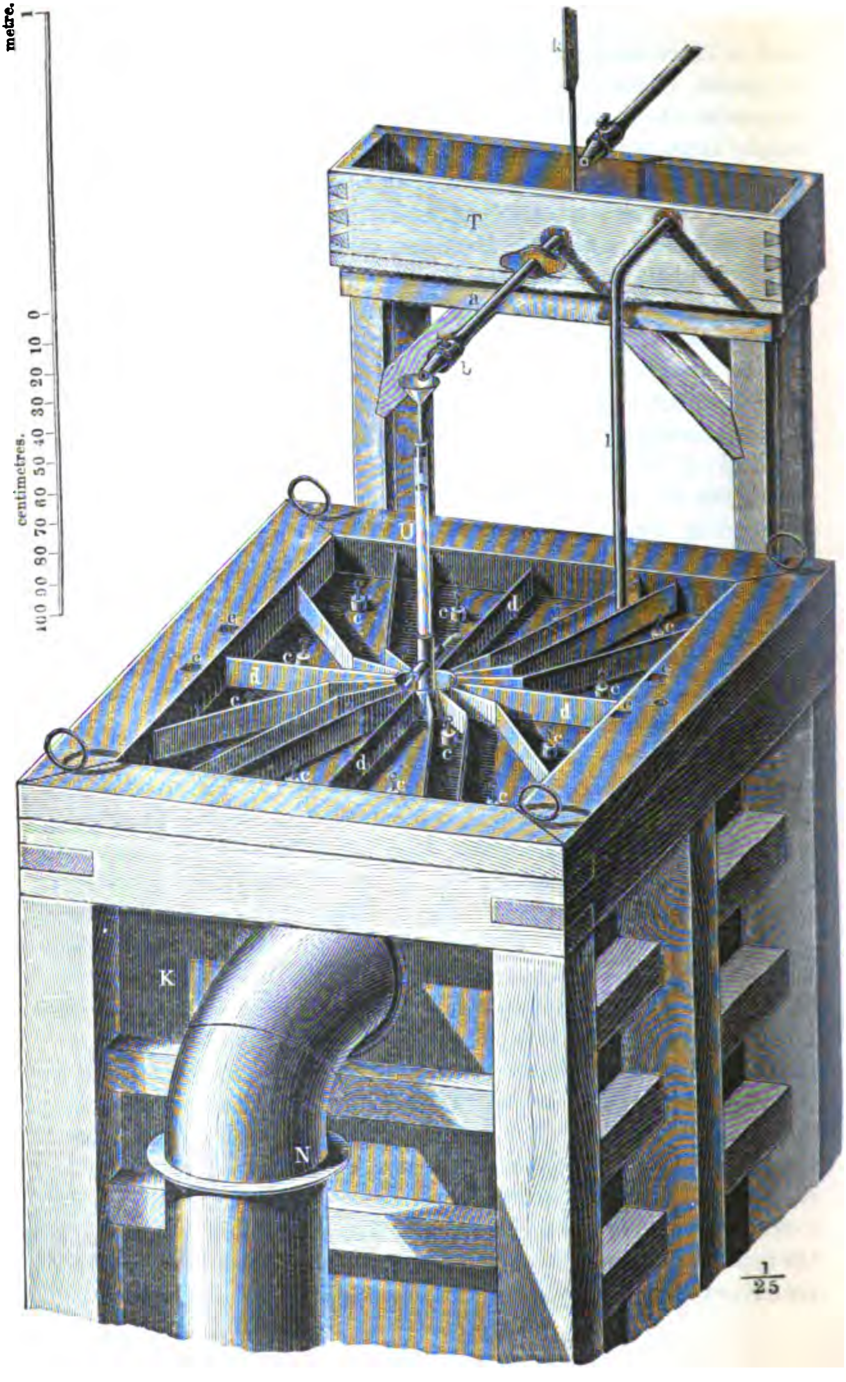
To return to the Freiberg towers, it should be noted that, for the observation of the colour of the gas before and after its passage through the tower, two glass panes are placed in each of the two valve-boxes L and O, opposite to each other; or a portion of each of the two tubes J and N may be made of glass. The gas ought to be of a ruddy colour before entering the tower, and perfectly colourless after leaving it.

In this process it is of great importance that the supply of sulphuric acid, which is to deprive the gases of their nitrous acid, be exactly regulated, and that from the beginning this acid be spread equally over the coke; otherwise too much sulphuric acid may be used, and the gas may pass through the tower without giving up the whole of its nitrous acid. Special care must therefore be taken in the construction of the apparatus for spreading the vitriol. In the Freiberg towers this apparatus consists of two leaden tanks, S and T (fig. 161), and the special distribuing arrangement fixed on the cover *g*. The vitriol is generally charged into the larger tank S from the lower part of the works by means of a pumping-apparatus, consisting of an air-tight vessel, into which air can be forced by means of a pump, which then forces the acid upwards through a pipe, *h*, reaching to the bottom of the vessel. This pumping-apparatus will be described in detail below. The pipe *h* ends at the tank S in a rose, *i*, made of "regulus" metal (a mixture of 5 parts of lead and 1 part of antimony); this rose serves for retaining any solid bodies suspended in the acid, and can be opened at the top in order to be cleaned. From the tank S the vitriol runs through a tube at its bottom into the smaller tank T; the supply into the latter is regulated automatically by means of a lead float suspended from an arm of the beam *k*, which in descending lifts a conical valve suspended from the other arm, that closes the running-off tube when the float rises too high. The tube *l* only serves for taking away any excess of acid in case of an irregular working of the float, so as to avoid any running over.

From the smaller tank, T, the vitriol runs to the tower *k*, where it has first to pass through the spreading-apparatus. An ordinary oscillating bucket was formerly used as such; but the quantity of acid employed is so small that the oscillations only took place at pretty long intervals, and too large a quantity of acid was then emptied out at a time; moreover the play of the bucket was often interfered with from mechanical causes. At most works, therefore, it is no longer used. Another arrangement (sketched in fig. 161) consists of four series of four dropping-tubes each, fixed in the top of the tower at equal distances; they are provided with a funnel at the top and a swan-neck bend at the bottom, inside the tower, so as to form a lute against the outside air by the liquid remaining in the bend. The vitriol is conveyed to these drop-tubes by the tube *o*, which divides itself into two arms, running each between two tows of the drop-tubes, and provided with a small tap for each of the latter, so that each small tube gets its special supply of acid. There are thus sixteen taps for the regulation of the flow of vitriol. This is a very faulty arrangement; for it is next to impossible to regulate them all so as to give a perfectly equal supply from each, considering the very small quantity of acid that has to pass through them; and both the taps themselves and the bends of the tubes are also very easily choked up.

For this reason another arrangement for distributing the vitriol, which was first applied at the Aussig chemical works by Mr. Schaffner, and has turned out entirely successful, is generally preferred. In this the supply of vitriol is regulated by a single tap, which can be opened wide enough not to be choked as easily as the sixteen small taps in the former arrangement. Fig. 163 (from Schwarzenberg) represents this apparatus on a scale of 1 : 25. In the top of the tower there are again sixteen holes, *c*, through which the vitriol trickles onto the coke below. Each hole has an upstanding rim about 1¼ inch in height, which is covered by a lead cap, nicked at the bottom in a few places to the depth of ¾ inch, so that the acid can pass through without hindrance. As soon as the top of the tower is covered with vitriol to the depth of that rim, the vitriol runs over into the inside of the tower; but no gas can escape through the holes, since they are luted with acid. The spreading of the vitriol is effected by a small reaction-wheel U, fed from the tank T by the tube *a* and the tap *b*, which regulates the supply. The lower part of the wheel and the two arms consist of lead; in this is fixed above a strong glass tube, and below another short glass tube, drawn out to a point which runs in a socket of glass or lead. One of the arms is also fitted with a glass tube, from which the vitriol runs out. There is a guide, consisting of two parallel rods of lead or of wood covered with lead, which rest on frames fixed in the holes *e e* of the top-frame, and on which four glass tubes are placed close to the upright column of the apparatus, so that they form a square within which the column revolves. As soon as the column is filled with vitriol, the wheel revolves regularly, the liquid running out of the open arm. On the quantity of the acid run in depend the height to which the column is filled and the velocity of its revolution. The axle of the wheel is exactly in the centre of the tower; and a cylinder of lead about 4 inches in height is burnt to the top of the tower, so as to prevent the acid from getting to the centre. From this cylinder sixteen radial ledges *d*, also made of

Fig. 163.


metre. 1
centimetres. 0 10 20 30 40 50 60 70 80 90 100
k
T
a
b
l
U
d
c
e
K
N
1/25

lead and burnt to the top-lead of the tower, branch off at equal distances. These are continued in a straight line as far as the periphery of an imaginary circle, beyond which the wheel cannot pour out any acid, and then alter their direction; so that between each two of them one of the above-mentioned sixteen holes is placed. Thus the top of the tower is divided into sixteen compartments, each of which contains an opening for running off the acid, and all of which are fed by the wheel with an equal quantity of acid.

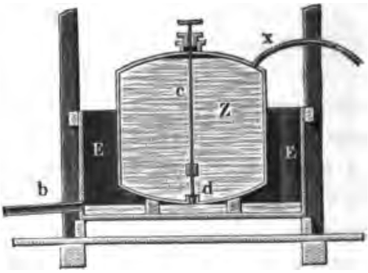
In England the spreading-apparatus is generally made altogether of lead; but the glass one, as figured by Schwarzenberg, is certainly more mobile. We shall, further on, give detailed drawings of spreading-wheels in the description of the Glover tower.

Since it happens now and then that the reaction-tube stops, especially with a small feed of acid, the arrangement of Seybel, at Liesing near Vienna, can be recommended, by which the wheel at each revolution strikes against a bell audible from below.

It is evident that the *regularity of the supply of vitriol* to the coke-tower is of the utmost importance for its good working. The whole acid-chamber process is so constituted that its course must be kept as continuous and uniform as possible, and the large bulk of the lead chambers in this case serves as a regulator, similar to the air-vessel of a blowing-engine, so that the gas, on leaving the chamber, issues, or at least ought to issue, with nearly absolutely uniform speed and composition. In similar spaces of time there will therefore be a similar quantity of nitre-gas leaving the chambers; and this in the absorbing-tower should always find the same quantity of vitriol, lest either there be an escape of nitre-gas or the nitrous vitriol come out too weak. But if the vitriol flows out of a tank, the opening of the tap remaining the same, the flow will be much quicker at the beginning, when the tank is full, than afterwards, when it is partly empty, and the tower will thus be fed very irregularly. The speed of outflow of liquids decreases in the proportion of the square roots of the heights of liquid in the tank; for instance, when the tank is filled to the height of 4 feet, the flow of acid will be twice as fast as when it only stands 1 foot high—both being cases which often happen in practice.

In order to secure a very regular supply of absorbing acid to the tower, several arrangements have been adopted, apart from that described above—for instance, Mariotte's vessel (shown in fig. 164), similar to that used in a kind of colza-oil lamps. The vessel Z is placed with its mouth downwards in an open basin E, in such a manner that its mouth is luted by the vitriol contained in the basin; therefore nothing can run out of Z. But as the vitriol

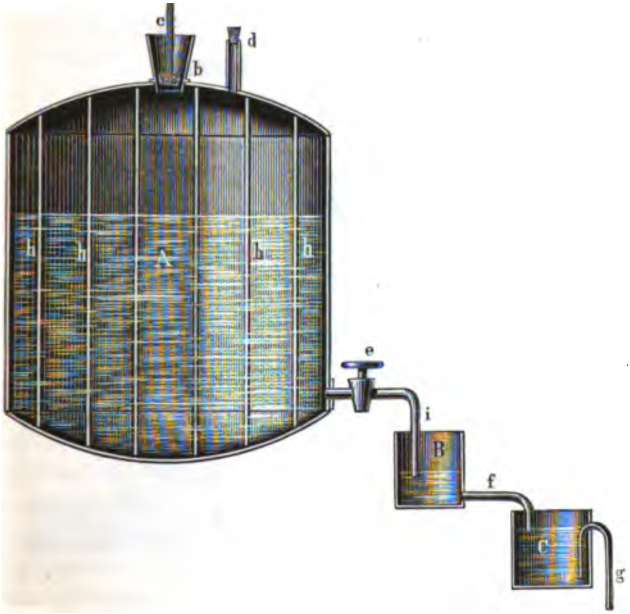
Fig. 164.



runs away from E through the pipe *b* onto the coke-tower, the level of E is lowered, the mouth of Z becomes free, a few air-bubbles enter, and acid flows out till the original level is reached, and the mouth of Z is luted again. The valve *d*, with the valve-rod *c* passing through a stuffing-box, serve for closing the mouth of Z during the time that this vessel is being fed through *x*.

In a simpler shape the same principle used to be applied some years ago in a few English alkali-works, as shown in fig. 165. A is a pretty large leaden vessel, protected against collapsing by iron rods covered with lead, connecting its top and bottom; these are required because the air in A is at a lower pressure than that outside, from which those vessels used to be called *vacuum-retorts*. They are filled through the funnel *b*, the air escaping through *d*; *b* is then closed tightly by the valve *c*, and *d* by a stopper. From the cock *e*, made of antimony and lead, which must close air-tight, proceeds a pipe *i*, which enters and descends about halfway to the bottom of the small vessel B. The latter has, at the bottom, an exit-tube, *f*, whose bore is a little smaller than that of *e*. When the cock *e* is opened, acid will run out and air will enter into A at the same time; but as the acid cannot run out of *f* as fast as it runs in, its level will rise in B, and as soon as it closes the mouth of *i*, no more acid can run out of A, because no air can enter; but as soon as a little acid runs out of *f*, a few air-bubbles will get into A, and a corresponding quantity of acid will run out; so that the level of the acid in B will remain nearly the same until A is totally emptied. The acid, therefore, runs out of *f* constantly under that

Fig. 165.

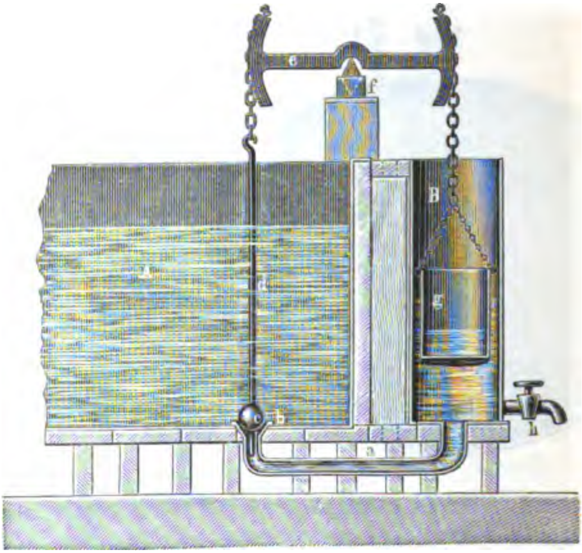


pressure which is determined by the vertical distance between the mouth of *i* and the junction of *f*—that is, in a uniform jet. It thus gets into the vessel C, and from this through the intermittent siphon *g* (comp. p. 318) into the coke-tower.

The vacuum-retorts have been abandoned again, because their action entirely depends upon no air entering the vessel A otherwise than through the cock *e*; in any other case the vessel B must run over, and the action of the apparatus as a regulator ceases altogether. It is, however, very difficult always to make a *perfectly* air-tight stopping at *b* and *d*; and therefore overflowing often happened. Besides, in consequence of the partial vacuum in A, air was apt to enter through the least fault in soldering the lead &c.

The object in question is better accomplished by the balancing apparatus shortly described above after Schwarzenberg; it shall now be explained in more detail. In fig. 166, A is the large acid-tank on the top of the coke-tower, made of wood lined with lead, which is filled from time to time. Beside it stands a lead cylinder B of equal height and 12 inches wide; the two communicate at the bottom through the lead pipe *a*. This pipe ends in A with a valve-seat *b* of hard lead, bored out in a taper shape. In this plays a ball valve *c*, also made of hard lead ("regulus"), which is continued below into a small guide-rod, and above into the lead-covered iron rod *d*, which projects above A, and is suspended by a short chain from one arm of the balancing-beam *e*. The latter swings with its centre on a steel edge *f*, and carries on its other arm, exactly over the cylinder B, another chain, from which a leaden bucket *g* is suspended inside B. Acid is poured into the bucket *g* until it sinks to a certain depth in the acid standing in B; by pouring in more or taking out some of the acid in *g* that depth, and with it the height of acid in B itself, can be regulated at any time: this bucket is therefore a form of float, preferable to the solid lead float figured by Schwarzenberg. The

Fig. 166.



bucket *g* is so weighted, and the length of the chain such, that at a certain height of acid in B the valve *c* must close the opening *b*. The valve *c* with the rod *d* and its chain is about as heavy as the float *g* along with its chain, and closes the opening *b* so long as a portion of the weight of *g* is neutralized by the upward pressure of the acid in B. As soon, however, as the cock *h* begins to run and the float sinks down, the rod *d* is raised by means of the beam *e*, and the ball valve *c* leaves the opening *b* free; thus acid flows across into B through *a*, lifts the float *g*, and *c* sinks down into its position, closing *b* again. Thus, by small oscillations of *e*, always the same quantity of acid will run out of B in the same time, as this only depends on the weight of *g* and the length of the chain, but is independent of the level of the acid in A. The ends of the beam *e* are shaped as segments of a circle, in order (by means of the chains) to convert their circular movement into a rectilinear one for the rod *d* and the bucket *g*.

The above apparatus, as it has hitherto been figured in books and carried out in many works, does not work well, and has even been given up in many places where it had been erected. In the first place, the beam is usually represented swinging on a pin which passes through its centre; but then the friction is very great, and soon becomes greater by the iron rusting, so that the beam sticks fast. This cannot happen if the arrangement is that shown in the above diagram, viz. a steel edge like those of delicate balances; when plated with nickel it remains free from rust. But, above all, the valve *c* ought not to be a truncated cone, as hitherto figured in the books. The guiding by the arc-shaped arms of the beam is not so absolutely vertical that a conical valve cannot now and then jam itself in its seat during its play upwards or downwards; in that case the apparatus ceases to work. If, however, the valve is ball-shaped, a slight deviation from the vertical does no harm, as it always closes the hole, and jamming fast is out of the question. Whilst those manufacturers who had erected the above-mentioned imperfect apparatus were mostly induced to give it up again on account of its constantly breaking down, the arrangement figured here works with the greatest ease and regularity, and can be highly recommended. At some of the largest works, from not being acquainted with the *right* way of making the apparatus, they have abandoned automatic regulation altogether, and leave it to the workmen to set the running-off tap of the acid-tanks according to the level of the acid—a very rude method, which, according to the explanation just given, there is no reason for retaining.

Whenever "lead-covered" iron rods are mentioned, it should be understood that for this purpose the iron rod is put into a pressed lead tube of convenient bore, and both ends of the latter are soldered up.

It will rarely be possible to feed the acid-tank on the top of the absorbing-tower with concentrated vitriol by natural fall; where the concentration takes place in the Glover tower, that possibility is excluded from the outset. There is therefore need for an *apparatus to force the acid up to the top of the absorbing-tower*; the same apparatus will also serve for forcing the nitrous vitriol and the chamber-acid to the top of the denitrating-tower. Ordinary force-pumps cannot be employed here, because these cannot be made without using metals which are acted upon by the acids, at least not for such quantities as have to be treated in this case. Fortunately we have two metals which resist the vitriol very well, viz. cast iron and lead, and with the aid of these an apparatus can be constructed in which the force-pump acts only indirectly, viz. through the compression of a column of air, which thus enters into the forcing-apparatus proper, and conveys the acid to any desired height. A similar principle has been employed long since in sugar-works, where there is an equally good reason for avoiding direct pumping, viz. that such pumps cannot be kept quite clean, and would spoil the sugar-liquors by the acids generated in them. The liquids are therefore pumped up by running them into a small upright steam-boiler, from whose bottom a delivery-pipe rises upwards, and by admitting steam at the top, whose pressure forces the liquid upwards in the delivery-pipe until the apparatus is quite emptied. As the liquids in sugar-works are mostly treated at a boiling heat, they are not excessively diluted by condensed steam.

In sulphuric-acid works it would not do to proceed precisely in the same way; for the strong acid would instantly condense the entering steam, and thus there would not only be no pressure upon it, but it would actually have a sucking action, and it would at the same time become very much diluted and very warm, and therefore useless for absorbing the nitrous gas. It has certainly been suggested (see Kerl-Stohmann's Chemie, 3rd ed., vi. p. 239) to connect the pressure-apparatus with another boiler, and to admit steam into the latter; it would then cause a sudden expansion of air in the second boiler, and this would press on the surface of the acid in the first boiler, and force it up in the delivery-pipe. If such an arrangement has really been introduced into practice, it must, for all that, be very little adapted to the purpose; there will be incomparably more steam used in this way than suffices for working an air-pump, and a portion of the steam will certainly pass over into the pressure-apparatus and dilute the acid within it.

The ordinary plan of working (introduced about 1838 by Harrison Blair, according to Richardson and Watts's 'Chemical Technology,' vol. i. pt. v. p. 217) is this, to convey air compressed by an air-pump or, more properly speaking, by a small blowing-engine into the pressure-apparatus, above the surface of the acid, exactly similar to the way in which every chemist in his wash-bottle forces the liquid up in the outlet-tube by blowing air in through another tube. In this there is no special limit of height, so long as the apparatus is made strong enough to resist the pressure and the air-pump is sufficiently powerful.

The air-pumps are generally constructed in this way:—The steam-cylinder and the air-cylinder are both fixed on a common horizontal ground-plate, or cast in one piece with the same; they are then worked by a common piston-rod with a piston at each end. A cross-head sliding between motion-bars gives the necessary guidance; and a pretty heavy fly-wheel secures regular action. The dimensions of the pump are chosen according to the size of the works; for a set of chambers of from 140,000 to 200,000 cubic feet a steam-cylinder of 8 inches diameter, an air-cylinder of 12 inches diameter, and a stroke of 18 inches, with from 40 to 60 revolutions per minute, suffice for pumping all the nitrous vitriol, concentrated acid, and chamber-acid. The compressed-air pipe in this case has 1¼ to 1½ inch bore. Much care has to be taken of the valves of these pumps: if they work with too much noise, they last only a very short time; but, in any case, a second pair must always be ready for putting on when the first give way. The author, at his works, sent the exhaust-steam of the engine into the steam-pipe for the chambers, the steam-boiler belonging to which worked at only 10 lb. pressure per square inch; thus the steam for pumping the acid was got for next to nothing, since only the difference of pressure before and behind the steam-cylinder had to be made good by consumption of fuel.

The air-pipe, which must be made of very strong lead tubing, is not conducted direct from the air-pump to the pressure-apparatus, because in that case acid would inevitably be squirted back into the air-cylinder and soon ruin the valves; but the air-pipe is carried upwards a distance of from 10 to 13 feet, and then as much downwards, before entering the acid-vessel. Close to the air-cylinder a small branch tube with a cock is soldered on, in order to let out the air when the pumping is finished. Sometimes there is also a pressure-gauge fixed to it: but this is not of much use; for, in the first place, it is soon destroyed by the violent oscillations at every stroke of the piston and by the acid fumes; and, secondly, the workman can judge much more conveniently than by looking at the gauge, from the noise of the pump and the valves, whether it works easily or heavy—that is to say, with much or little pressure.

The acid-vessel serving as pressure-apparatus is made in various forms. At the commencement (and even now in many places) it was made in the shape of a soda-water bottle, as shown in fig. 167, afterwards as a horizontal cylinder (fig. 168) with bolted-on covers;

Fig. 167.

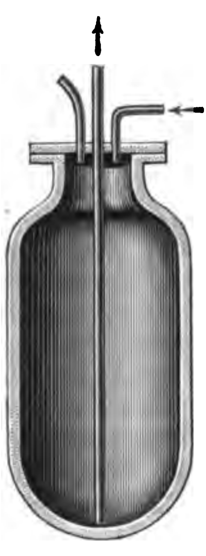
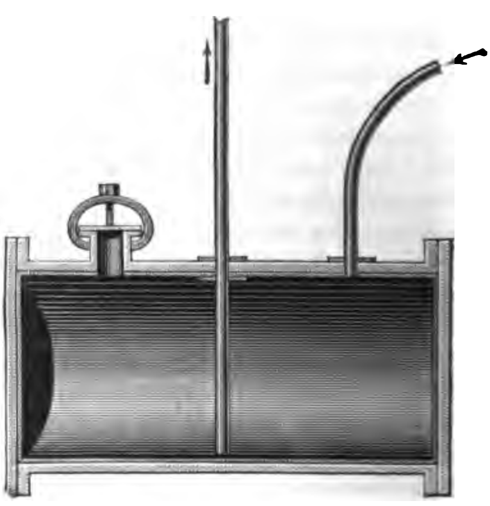
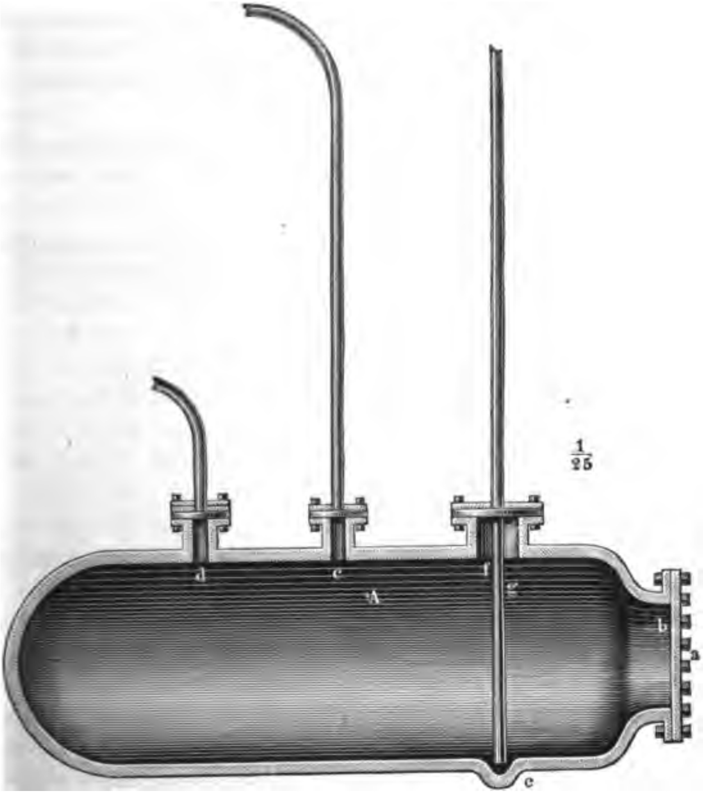


Fig. 168.



but it is now more usually as shown in fig. 169, a horizontal cylinder with one semicircular and one neck-shaped end, the latter closed by a man-hole door. These vessels are called "acid-eggs." The vessels like fig. 168 are usually lined with lead; those like figs. 167 and 169 are not. In England experience has everywhere shown that it is needless to protect the cast-iron of the acid-egg by a lining of lead; even the nitrous vitriol and the chamber-acid of 122° Tw. act so little on cast iron that such a protection becomes unnecessary. The author has found an acid-egg, after five years' continuous use for all three kinds of acid, in entirely good working-order. Lining with lead has this drawback, that as soon as a little

Fig. 169.

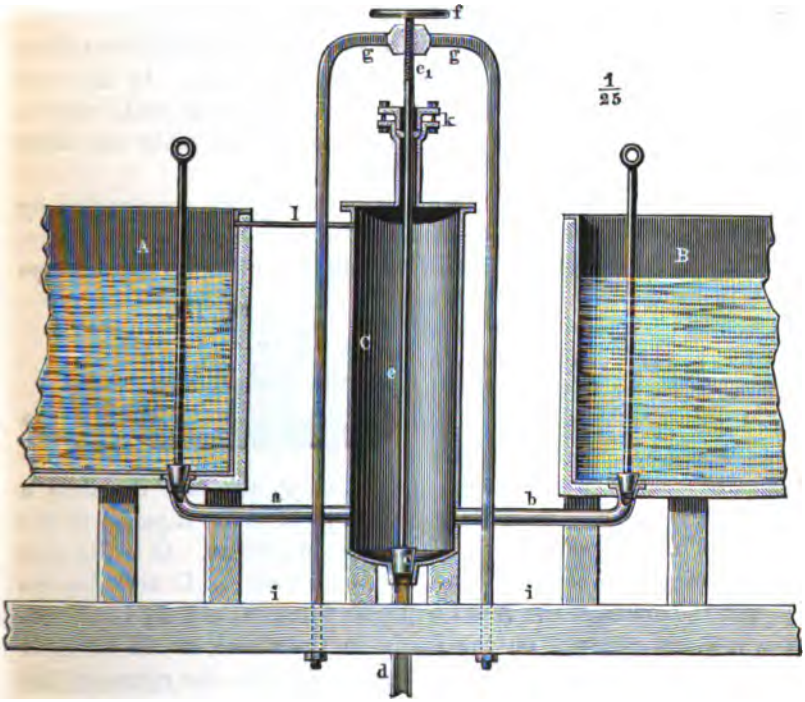


air enters between the lead and the cast iron by the smallest possible chink the lead is driven away from the iron in many places, and its protecting action becomes quite illusory, whilst the contents of the egg are diminished.

The horizontal has the advantages over the vertical shape:—first, that no well is needed for the acid-egg, which may lie on the floor and thus be accessible all round; secondly, that in the case of excessive pressure, the weakest part (viz. the man-hole) being situated sideways, the acid squirting out is not so likely to do damage to men and machinery as in the case of squirting out vertically, especially if the cylinder is at once laid with the man-hole turned away from the machinery.

In fig. 169, A is the acid-egg, whose walls are 2 inches thick; *b* is the neck, with the man-lid *a* fixed to it by bolts and nuts; a thick india-rubber washer makes the joint tight; *c* is a recess at the bottom of A, into which the delivery-pipe *g* projects, in order to expel the contents of A as completely as possible; *d, e,* and *f* are three branch pipes, *d* for introducing the acid, *e* for the air-pipe, and *f* (the widest of them) for the delivery-pipe. The pipes have each a strong lead flange soldered to it, which rest on the flanges of the branches *d, e, f*; by putting loose iron washers on the top, and screwing all three together by bolts and nuts, the joint becomes perfectly tight. The inlet branch *d* may be left open and closed after each filling by a small plate bolted on; but in most cases there is an inlet valve for the acid, of the shape shown in fig. 170. (The plain stoppers with lever-rods, figured in Muspratt's 'Chemistry,' cannot support any great pressure.) A and B are acid-tanks, which need not be placed so close to the pressure-valve C as they are represented in the diagram. C is a cylinder of strong lead, about 10 inches wide, whose top is at a level with the top of the tanks, but which is deeper than these, so that they may communicate with C through the pipes *a* and *b*, connected with their bottoms. *a* and *b* end in the bottoms of the tanks with valve-seats of "regulus" metal, and are usually closed by taper valves with long lead-covered handles: there is no pressure upon these exercised from below; and therefore they need not be provided with any special contrivance against this. When it is necessary to run the contents of these two tanks, or that of a third tank, not visible in the diagram, but similarly communicating with C, into the acid-egg, the respective bottom-stopper is taken out, the bottom-valve *c* in C also remaining open. The latter valve, which must be very well ground into its regulus seat, communicates through the pipe *d* with the corresponding inlet branch of the acid-egg. On the top it is connected with the lead-covered iron rod *e*, which ends above in a screw-worm e', and can be turned by means of the hand-wheel *f*. A very strong iron frame, *g g*, with

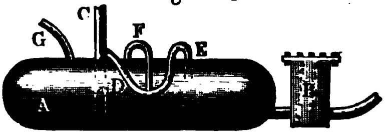
Fig. 170.



a female thread corresponding to the worm e', is bolted to the bottom-joists, *i i*; both the timber and the iron rods must be very strong, as there is a good deal of strain upon them in screwing the valve in and out. As the cylinder C is equal in height to A and B, it can never run over; and when the acid in C stands at the same level as that in the tank, the valve *c* is screwed down tightly by means of the hand-wheel, the corresponding stopper is put into its seat in the tank, and the air-pump is started. The whole pressure of the acid, which has sometimes to be lifted to a height of 100 feet, will then act from below on the valve *c*; and unless the latter has been screwed down perfectly tight, the acid will squirt out vehemently. Although, with a little care on the part of the workman, this should never happen, yet several accidents caused by men being splashed with acid have led to providing the cylinder with a cover and a stuffing-box, *k*, through which the rod *e* passes; the splashing does then no harm, as the acid cannot get out. At the same time the stuffing-box serves as a guide for the valve-rod, which would otherwise have to be provided in some other way. Sometimes (not always) there is a small pipe provided for taking any acid squirted out into one of the three tanks. In this way the same acid-egg can serve for pumping strong acid, nitrous vitriol, and chamber-acid out of their respective tanks one after another.

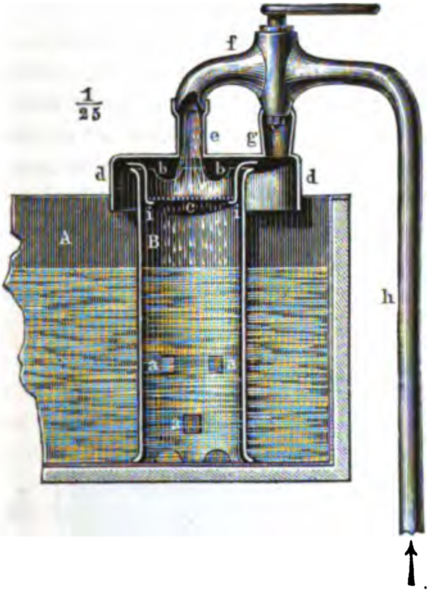
A self-acting apparatus for filling the acid-eggs, constructed by Mr. Harrison Blair, which, Mr. Mactear says (Journ. Soc. Arts, 1878, p. 558), works well, is shown here according to the description in Richardson and Watts's 'Chemical Technology,' vol. i. part v. p. 217. A (fig. 171) is a strong cylinder of lead closed at both ends [probably cast iron would be preferable]; B a valve-box, and C a delivery-pipe, into which the pipe D enters a little above the vessel. D is continued to E, where it passes to the inside of the vessel, and joins D at the lowest part. G is the pipe which brings the air from the pump. So long as D contains no liquid, the air from the vessel will pass through, and by thus preventing any pressure on the liquid in the vessel, it will be filled through the valve-box. When the vessel is full, the egress of the air through F being stopped by the liquid, the latter will be forced up E (being lower than F), which, acting as a siphon, fills D and effectually stops the passage of air. As the pressure of air increases, the liquid rises up the delivery-pipe and is conveyed to any required point, while the liquid in D falls with the level of that in the vessel, until this sinks below the bend in D, when the air rushes through, carrying with it all the liquid out of D. This leaves a free passage for the escape of air during the time the vessel is again being filled, the air-pump working the whole of the time.

Fig. 171.



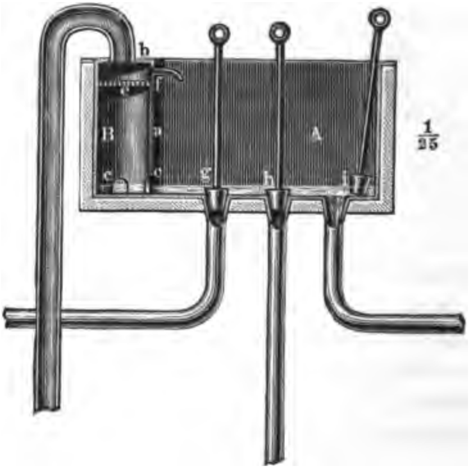
As soon as, in the ordinary kind of apparatus, the pumping is finished, the air-pump, to which now no resistance is offered, begins all at once to go extremely fast, and draws by its noise the attention of the workman to the necessity of stopping it. Directly after, the air-cock in the pipe conducting the compressed air to the acid-egg is opened. Nevertheless some compressed air accompanies the last portions of the acid and rushes vehemently out of the top of the delivery-pipe; and in order to prevent the acid from being thrown about a special contrivance must be adopted, for instance that shown in fig. 172. A leaden cylinder, open at top and bottom, stands within the tank A; it is jagged out at the bottom in a few places; and the holes *a a* higher up also help to give free communication between B and A. Also the top of B is cut out pretty deeply in a few places (*b b*). Within B the perforated plate *c* is suspended by a few lead strips, *i i*; the whole is covered by a loose cover *d d*, which is kept at a little distance from the top of B by the lead strips, so that the air can escape between them. *d* has a flange of 8 in. depth; in the centre it

Fig. 172.



carries a short tube *e*, to which the "regulus" cock of the delivery-pipe *h* is burnt. Since it is extremely difficult to keep such a cock tight, especially under great pressure, it is surrounded below by the pipe *g*, which also joins into *d*, and thus carries away the droppings. This contrivance acts in the following way. When the acid forced up through *h* arrives at the top, it runs through *f* and *e*, then through the sieve *c* and into the cylinder B, whence it easily passes through into A. But in the last stage, when compressed air arrives at the same time with the acid, the latter cannot be squirted about, nor can the current of air act upon the surface of the acid within the tank so as to splash it about; for it is broken by the sieve *c* and escapes through the openings of *c* and the annular space below *d* without doing any damage; the acid accompanying it runs quickly down through the sieve *c*. The cock *f* and the pipe *g* are required only when a single acid-egg has to feed several tanks placed at a considerable distance from each other, for instance one on the absorbing-tower and two on the Glover tower; for then the delivery-pipe must be divided into two parts, and each must be provided with a stop-cock, only that leading to the working tank being opened. If, however, the tanks to be filled are placed close together, no cocks are required, but the simpler arrangement, fig. 173, can be employed, which can also be made much smaller than (for the sake of clearness) it has been drawn here. Within

Fig. 173.



the same lead-lined box A there is a special compartment B constructed by means of a lead partition, *a*, and cover, *b*. The side of B is jagged out at the bottom at *c c*, in order to communicate with A. The delivery-pipe joins into the cover *b*; the air rushes against the sieve *e* and escapes out of the pipe *f* without doing any harm. In the bottom of A there are three valve-seats, *g*, *h*, and *i*, connected with as many pipes leading to different tanks; but only one of the valves is left open at a time; the two others are closed by plugs, and the tanks communicating with them therefore receive nothing.

In smaller works there is usually only one acid-egg, which serves for pumping all the strong acid, nitrous vitriol, and chamber-acid, one after another. In this case the air-pump has nothing to do during the time that the egg is getting filled from one of the tanks; but if the cubic contents of the chambers do not exceed 200,000 cub. feet, there is time enough for that. But where the chamber-space is larger, there will be at least two acid-eggs required, of which one usually serves for the strong acid and nitrous vitriol, the other for the chamber-acid; in that case the same air-pump can do all the work if the air-delivery pipe is provided with two branches and two stop-cocks, one of the eggs always getting filled whilst the contents of the other egg are being pumped up; the air-pump is thus fully utilized.

Instead of the Gay-Lussac coke-tower in some works, but rarely in large ones, and altogether only exceptionally, absorbing-apparatus similar to *Woulfe's bottles* are used. Such an apparatus is represented, after Schwarzenberg, in figs. 174 & 175, in elevation and plan, on a scale of 1 : 50. It consists of from 30 to 40 jars, *k*, about 3 feet high, made of stoneware and well burnt. They are connected together by pipes made of the same material, which are put into the necks, *c*, and made tight with oil cement. The gas from the last lead chamber is deprived of moisture as much as possible in the box *a*; it then traverses the jars, which are filled to about one third with vitriol of 152° Tw.; the gas yields up its nitrous acid to the vitriol, and is carried away at *d* into a chimney. In order to fill the jars more conveniently, funnel tubes, *h*, are put in through the openings *f*, which reach down almost to the bottom of the jars, so that they are luted by the vitriol: the latter is run off by the cocks *g*. The vitriol remains 24 hours in each series of the jars. The first series is emptied daily; and each jar is filled up again with the contents of the corresponding jar of the second series; the jars of the

Fig. 174.

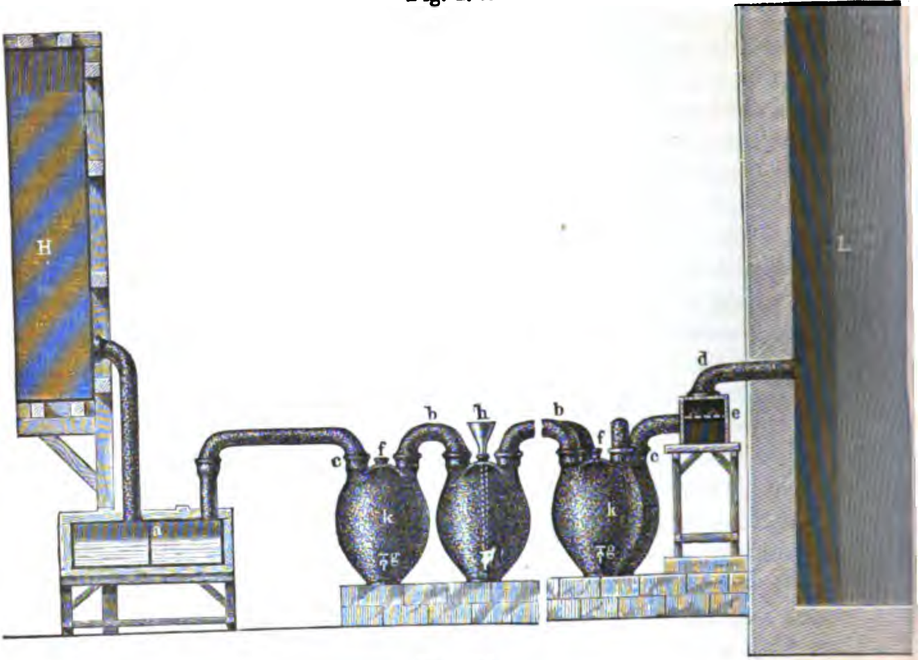
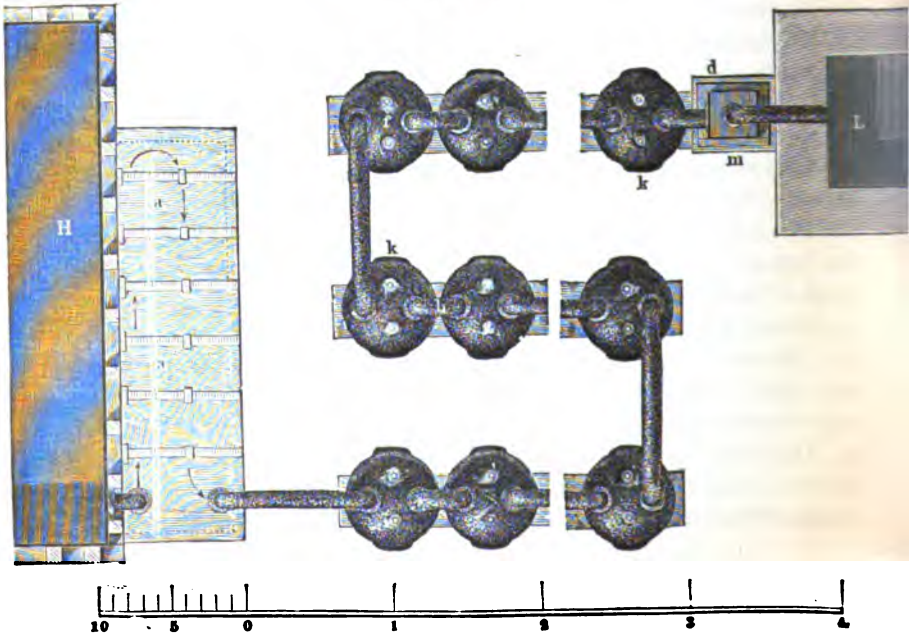


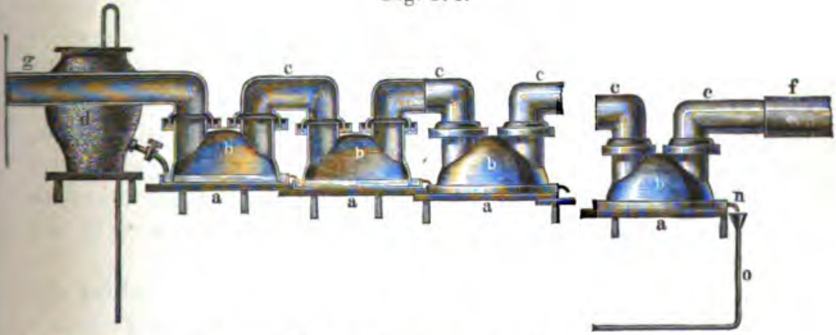
Fig. 175.



second series receive the contents of the third, and the latter fresh vitriol. To facilitate this, the second series should be placed at a higher level than the first, and the third series higher than the second, so that the acid can run away at once into the jars of the next lower series. A special tank feeds the top series.

In the place of Woulfe's jars some works use large dishes, *a*, fig. 176, covered with bell-jars, which are connected by wide pipes, *c*.

Fig. 176.



This arrangement has the advantage that the single pieces of the apparatus can be made more easily and cheaply and of larger size, and that the vitriol flows by itself through all the dishes of the apparatus, which are placed terrace-wise, in a direction opposite to that of the current of gas.

This kind of apparatus is certainly much cheaper than coke-towers, but is so inferior to them in its absorbing action that it is not at all adapted for a large scale of working.

After the above explanations very little need be said *on the working of the absorbing-tower*. The following points have to be observed in this:—

The *gas* entering the tower must show a distinctly red colour in the "sight;" on the other hand, the exit "sight," behind which a board painted white ought to be placed, should show a perfectly colourless gas. The gas escaping from the top of the tower, or of the chimney connected with it, ought not to produce red vapours when it meets the outer air. Furthermore the chamber-gas before entering the tower should be as *dry* and as *cool* as possible, lest the absorbing acid be diluted or heated. For this purpose the last chamber receives very little steam, so that its acid remains at about 106° Tw.; moreover the gas is often conducted through a

Fig. 174.

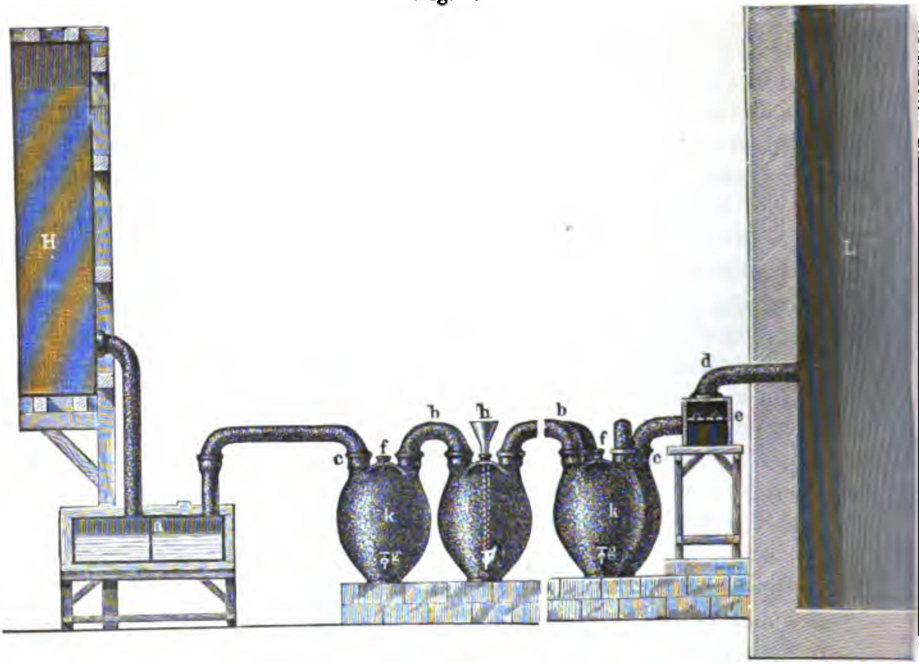
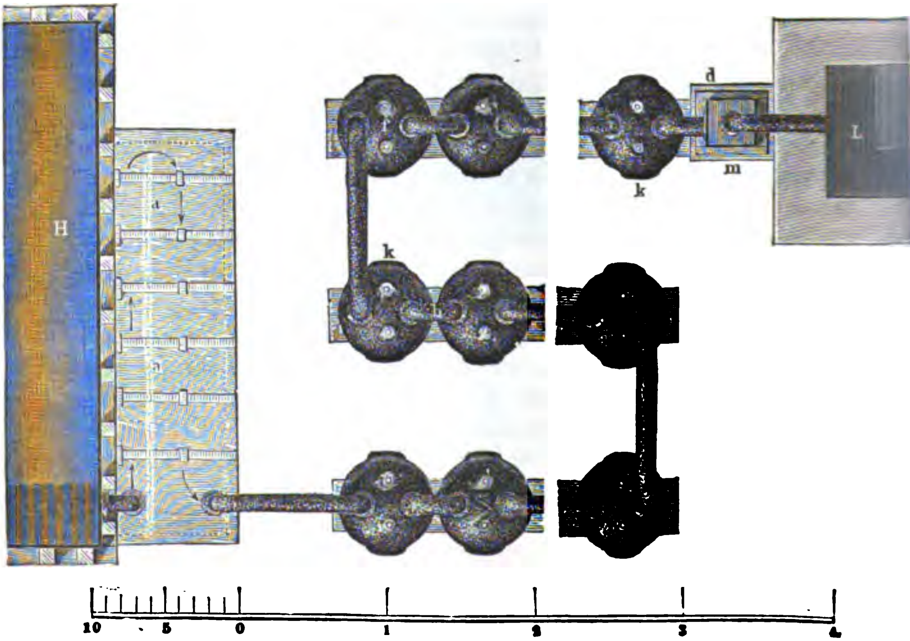


Fig. 175.



second series receive the contents of the third, and the latter fresh vitriol. To facilitate this, the second series should be placed at a higher level than the first, and the third series higher than the second, so that the acid can run away at once into the jars of the next lower series. A special tank feeds the top series.

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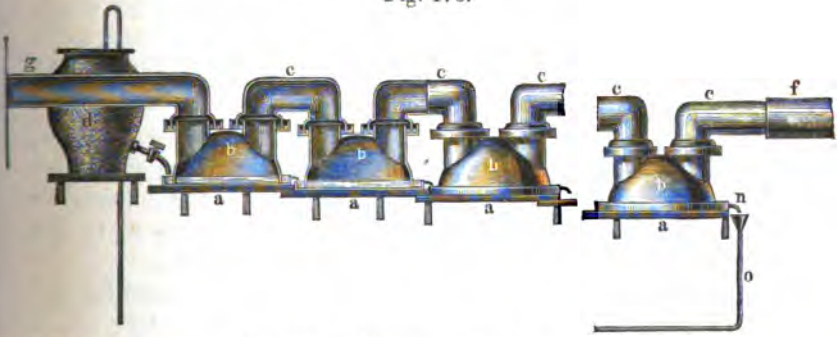
Fig. 176.



This arrangement has the advantage that the single pieces of the apparatus can be made more easily and cheaply and of larger size, and that the vitriol flows by itself through all the dishes of the apparatus, which are placed terrace-wise, in a direction opposite to that of the current of gas.

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Above every thing care must be taken that the acid used for absorbing is as *cool* as possible. Hot acid absorbs very badly; much nitre is lost (especially, according to Winkler, hyponitric acid, more than nitrous acid); and at the same time a weak nitrous vitriol is produced. It is therefore necessary either to provide a very large tank for cooling the vitriol concentrated in pans or in the Glover tower, before it is employed in the Gay-Lussac tower; or, as the cooling by mere exposure to the air is a very slow process, especially in summer, and in large works enormous tanks would be required for it, special cooling-apparatus is employed. As such many works use double spouts—an outer one filled with water, and an inner one, in which the hot acid runs. In this case it is rarely possible to apply the rational principle of running the cooling water in a current opposite to that of the acid to be cooled, because, on account of the length of the spouts, there is no fall for this. Such double spouts also have a disagreeable tendency to swell out at the bottom whenever a little more pressure takes place, because the lead when hot loses part of its strength, which in any case is not considerable. This drawback can be avoided by the arrangement sketched in fig. 177, viz. by attaching to the spout, at about every 30 feet of its length, a tube rising perpendicularly from the double bottom through the upper spout and bending over the side of the latter; the

Fig. 177.

water can issue out of this, in case of stronger pressure, without mixing with the acid. The upright tube also serves for the escape of the air-bubbles which are often contained in the water, and which may stop the stream as well as cause the spout to bulge out.

Among the various contrivances for cooling the strong acid, which, in spite of their great diversity, have nearly all one common feature, that of an extreme liability to break down, the following apparatus is at English works considered one of the most practicable. Fig. 178 shows a sectional elevation through the line AB of the plan; fig. 179, a section through CD; fig. 180, a sectional plan. The diagram is on a scale of 1 : 25; but the cooling-trough and its pipes, as a rule, must be longer than represented here (in order not to extend the diagram too much). For a weekly make of 100 tons of acid, for instance, the trough ought to be 20 feet long. It is 4 feet wide and 2 feet high, and lined with lead; two vertical lead partitions divide it into three compartments—two small ones, *a*, *b*, at the ends, and one large one, *c*, in the middle. *a* and *b* con-

Fig. 178.

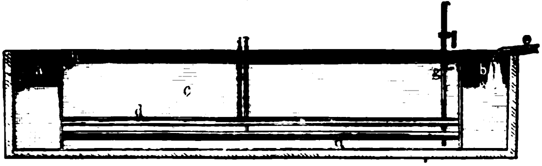


Fig. 179.

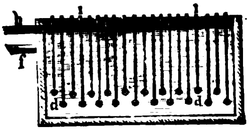
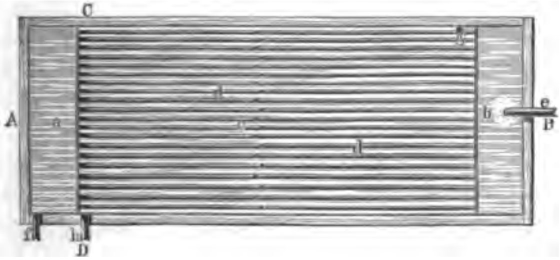


Fig. 180.



tain acid, *c* water; *a* and *b* are connected by about 20 lead tubes, *d d*, of 1¼-inch bore, which are burnt into the cross partitions and stay them at the same time, so that the partitions can easily resist the pressure of the liquids. The hot acid runs in through the pipe *e*, collects in the compartment *b*, and runs across to the compartment *a* through the pipes *d d*, in order to run away through the pipe *f*. Cold water runs into the inner box *c* through *g*; and the hot water leaves it again through *h*. The flow of acid through the great number of pipes is only slow; and the acid thus has time to give up its heat to the cooling-water. The vertical tubes, *i i* (3½ inches wide), attached one to each of the tubes *d d*, and projecting above the level of the water in *c*, serve for giving an outlet to the gas going along with the hot acid, and also for blowing through the pipes in cases of stoppage. This apparatus, which was first constructed by Mr. Stuart, now of the Hebburn alkali-works, is usually emptied and cleaned and examined every three weeks; the cooling-water should be daily tested several times for acid with litmus-paper. The acid is thus easily cooled down from 130° C. at *e* to 37° C. at *f*, and can be used for absorption at the latter temperature without any fear, whilst even at 50° C. its absorbing-power is sensibly less, and of course still less at a higher temperature. In another, larger manufactory, there is a trough of 100 feet length by 4 feet wide; the acid, first cooled from 132° down to 100° C. in a double spout, is further cooled in the trough down to 15° C., the apparatus cooling the acid for three sets of chambers of 140,000 cubic feet each.

A much simpler but perfectly efficient cooling-apparatus exists in the works at Aussig, Stolberg, and others. The acid runs out of the Glover tower immediately into a cylindrical trough of thick lead, about 2 feet high and wide, and runs out of it again through a pipe coming away from its bottom and turned upwards. In the trough there is a narrowly wound lead coil, through which cold water is continually running from above; getting heated in the bottom part of the coil, it rises up and is taken away hot at the top. The cooling here generally goes down to 40° C., and is supplemented by letting the acid stand in tanks; but 30°–35° C. might easily be attained. This is a very rational method of cooling, because the hot acid running in at the top comes into contact with the upper, hot part of the water-coil, whilst the acid ultimately flowing away from the bottom, which is already cooled down to a great extent, is cooled still further by the cold water in the bottom of the coil.

In ordinary circumstances the absorption in the Gay-Lussac tower requires at least one half of all the acid produced. This is got from the Glover tower without any other cost but that of pumping up; in the case of other denitrating apparatus the cost of concentration has to be added to this. Frequently the necessary quantity of absorbing-acid is stated at a lower figure—for instance, as one third of the whole production; but this in most cases is certainly insufficient, and no doubt a large loss of nitre would be the consequence of it. On the other hand, manufacturers working with Glover towers, who, apart from the trifling expense of pumping, have no concentrating-expenses at all, send all their acid once a day through the Gay-Lussac tower. This is quite right. Bode ('On the Glover Tower,' p. 49) calculates that, with a loss of 4 parts of nitre or 1·75 of N_2O_3 to 100 parts of acid of 170° Tw., the absorption requires at least 56 per cent. of *all* the acid of 144° manufactured, if very strong nitrous vitriol (with 1·75 per cent. of N_2O_3) is to be obtained. Such strong nitrous vitriol, however, is not obtained in ordinary working; and therefore considerably more than 56 per cent. of all the acid manufactured must be run through the Gay-Lussac tower in order not to lose any nitre.

The *nitrous vitriol* (that is, the acid issuing at the foot of the Gay-Lussac tower) should only be about 2° Tw. weaker than the strong acid fed in at the top; otherwise too much moisture has got into the tower. It is essentially a solution of chamber-crystals (nitrosulphonic acid) in sulphuric acid; but it may also contain a little hyponitric or nitric acid. According to some chemists it contains considerable quantities of the latter acids (hyponitric acid, or rather nitrogen tetroxide is in no case present as such, but at once decomposes into nitrous and nitric acids); but the author has found the contrary in all the nitrous vitriols analyzed by him. When properly treated, nitrous vitriol ought to be very little coloured, and ought to smell very little of nitrous acid; but on being diluted with water, especially hot water, it ought to effervesce strongly and to give off thick red vapours. At a few works this rough test is considered sufficient for judging of the quality of the nitrous vitriol; but at all the better works it is properly tested in the laboratory, according to one of the methods described in a previous chapter (p. 59 *et seq.*), which can be accomplished in a very short time; the best are the permanganate and the mercury methods. With the help of these it can be seen from day to day whether the percentage of nitre increases or decreases. In the former case, if the other tests of the chamber-process agree with it, this is an intimation that some of the nitre must be taken off; in the latter case this test will, better than any other, show, before any damage has been done, that more nitre is wanted. In any case nitrous vitriol ought not to contain less than 1 per cent. of N_2O_3; above 2½ per cent. it is too strong, and there is danger of nitrous gas escaping without being absorbed, which can be controlled by the colour of the exit-" sight." In this case more strong acid must be charged at the top; and if there is an excess of nitre-gas in the chambers, a little less nitre must be used.

The exact composition of nitrous vitriol has been determined by several chemists. Winkler found in a tower-acid of the Halsbrücke works (near Freiberg):—

Sulphuric anhydride	60·200
Water	37·191
Nitrous acid, N_2O_3	2·550
Nitric acid, N_2O_5	0·256
Organic colouring-matter	0·022
	100·219

Kolb (Bull. Soc. Mulhouse, 1872, p. 235) gives the following analyses:—

Density of acid	1·714	1·721
Sulphuric acid, SO_4H_2	76·7	75·8
Nitrous acid, N_2O_3	1·6	3·17
Nitric acid, N_2O_5	0·9	1·14
Lead sulphate, $PbSO_4$	0·006	traces

These results can hardly be accepted as certain, so far as the nitric acid is concerned, since the author has shown (Chem. News, xxxvi. p. 147) that the nitric acid found by Winkler and Kolb has probably been generated during the analyses, as Winkler himself considers to be possible. The author found, both in artificially prepared nitrous vitriol, and in samples obtained from the Uetikon works near Zürich, from the Dienze works in Alsace-Loraine, and from the works of G. C. Zimmer near Mannheim, no nitric acid whatever, but merely nitrous acid—for instance, in the acid from Uetikon, whose spec. grav. at 15° C. was 1·691, 2·44 per cent. (by weight) of N_2O_3, corresponding to 5·46 per cent. of nitrate of soda. Latterly Hurter (Dingler's Journal, ccxxvii. p. 472) and Davis (Chem. News, xxxvii. p. 125) assert that they have found more or less NO_2 in nitrous vitriol; but the mode of testing may have affected the result here also.

The success of the working of the Gay-Lussac towers depends above every thing upon the proper *regulation of the draught*. If the draught is insufficient, the chamber-process will from the outset be injured by the continual leakage of gas and by all the other drawbacks enumerated before, and especially by the behaviour of the pyrites in burning. In that case the Gay-Lussac tower itself will not work properly; for unless oxygen be present in the last chamber before the gas leaves it, there will be unoxidized nitric oxide left, which will pass through the tower unabsorbed and only form red vapours when issuing into the outer air. At the same time there will be sulphurous acid present in this case; and this acts still worse, since it decomposes the nitrosulphonic acid still present in the vitriol with which the coke in the tower is soaked, and carries away its nitre as nitric oxide. If the waste gas, as previously insisted upon, contains 5 or 6 per cent. of free oxygen, the above cannot happen to an appreciable extent, except in the presence of much arsenious acid (see Chap. XV.).

If, on the other hand, the draught is too strong, therefore with poor kiln-gas, the sulphurous acid will not have time to condense within the chambers as sulphuric acid; it will partly get into the tower, and there cause the decomposition just mentioned and loss of nitrous compounds.

In both cases, therefore, the same consequence will happen as if the last chamber did not contain an excess of nitre-gas; and if nitre is too much economized, it will indeed be wasted all the more in the way just described, the sulphurous acid driving off the nitrogen of the tower-acid into the air in the shape of nitric oxide.

Such a faulty working of the tower will announce itself by the escape of red vapours out of the chimney, by the tests of the tower-acid, and even by its appearance, since the vitriol, which otherwise is nearly or quite colourless, turns of a dark purple, and is filled with countless small bubbles of nitric oxide, at the same time getting heated by the formation of sulphuric acid (Bode, in a note to the translation of H. A. Smith's pamphlet, p. 122). It is therefore the worst case of all, if alternately sulphurous acid gets into the tower and the reverse. In that case nitrous vitriol is alternately produced and decomposed again. When, however, sulphurous acid constantly passes into the tower, there is no absorption of nitre-gas at all, and the tower in this case does not act as an absorbing apparatus, but simply as a continuation of the chamber-space (Bode, ib. p. 124). This proves, as Bode justly remarks, that one improvement, viz. the recovery of the nitrous acid, necessarily led to another, viz. to a better condensation of the sulphurous acid, or a better yield on the sulphur burnt.

Merely for the sake of completeness be it mentioned that several *other plans* have been proposed for utilizing the nitre-gas escaping from the chambers. Not one of them has ever possessed any practical value; and they can hardly be said to possess even an historical value, since they have never been employed except in a few isolated cases. Kuhlmann, for instance, employed 30 Woulfe's bottles, the first ten of which were filled with water, the second ten with a solution of barium nitrate, and the third ten with barium carbonate suspended in water; the mixture resulting in the last ten bottles was used in the second ten bottles, where barium sulphate ("permanent white" or "blanc fixe") was precipitated. Others have used milk of lime, ammoniacal liquor, or even pure water for the absorption of the acid vapours. All these plans are so very much less advantageous or complete than Gay-Lussac's process that they cannot at all compete with it.

Denitration of the Nitrous Vitriol.

The operation going on in the Gay-Lussac towers, or in the jar apparatus serving for the same purpose, and whose final result is the production of an acid more or less charged with nitrous compounds, viz. the "nitrous vitriol," requires for its necessary complement another operation, by which the nitrous vitriol, which by itself has no practical use, can be reintroduced into the chamber-process, both in order that the absorbed nitrous compounds may be restored, and that the sulphuric acid originally employed may be recovered in a pure state. It cannot be denied that Gay-Lussac was not sufficiently successful in completing his invention (which has been so important and useful for the manufacture of sulphuric acid) in this particular; and it is more than probable that the slow spread of his process, nay, even the far from exceptional abandonment of it where it had been introduced in the first instance, must be attributed to the fact that the denitration of the nitrous acid was attended with too many difficulties, expenses, and breakdowns of apparatus. The invention of the *Glover tower*, which does away with all this, must therefore be considered almost equally important with that of the Gay-Lussac tower itself; and in fact the *general* introduction of the latter only dates from the time when manufacturers were able to combine it with the Glover tower.

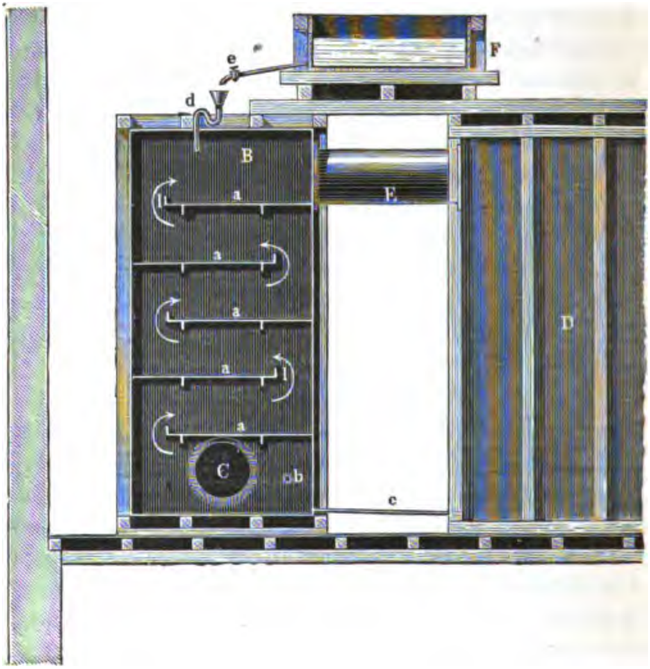
The various contrivances for denitrating nitrous vitriol have been described and criticised thoroughly and in detail by Fr. Bode, in 1876, in a paper "On the Glover Tower," which obtained the great prize of the Berlin Society for the Promotion of Industry; and this essay has been used to a great extent in the following description. Bode's paper has also been published by instalments in 'Dingler's Journal,' vols. ccxxiii. to ccxxv.

The methods for denitrating nitrous vitriol are founded, on the one hand, on diluting it either with hot water or steam, or with a combination of both, or, on the other hand, on the action of sulphurous acid, mostly along with a certain amount of dilution. That in these cases the nitrosulphonic acid is completely decomposed, either by the dilution or the action of the sulphuric acid, has been proved in detail at the beginning of this Chapter from theoretical investigations. We shall now treat of the apparatus and modes of procedure employed in practice for that purpose.

One of the oldest apparatus was described in Payen's 'Chimie Industrielle,' and has been copied out of this into most text-books; it may be called the "shelf apparatus." It is described in Schwarzenberg's work as follows:—

"This operation can be carried out in a small lead chamber, shown in fig. 181 in section at B. The nitrous vitriol is first conveyed into the tank F, placed above the chambers, and from this flows into the chamber through the cock *e* (by which its flow is regulated) and the bent funnel tube *d*. The chamber is provided with horizontal shelves, *a*, over which the acid runs down. They are burnt to the chamber-walls on three sides; and on the fourth side there is a small upstanding margin, *l*, for retaining a layer of liquid about 4 inches in depth. The gas enters the chamber direct from the sulphur-burner through the tube C, a little above the bottom of the chamber; the pipe *b* introduces the necessary steam in the same place. The latter decomposes the

Fig. 181.



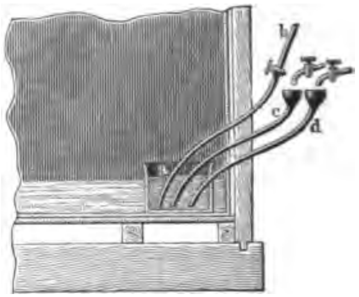
liquid standing on the shelves *a*, whilst passing over its surface, carrying along the gases. On the top the gaseous mixture, along with the nitrous acid set free, passes through the pipe E into the large lead chamber, whilst the sulphuric acid deprived of nitrous acids runs through *c* into the bottom of the same chamber."

Another apparatus, constructed on the same principle as that just described, is the "Dénitrificateur" proposed by Gay-Lussac himself. It is a lead column of square or circular section, provided with a grating a little above the bottom, and packed with coke on the top of this. The nitrous acid runs in at the top, and is scattered by means of a rose. Below the grating the gas of the sulphur- or pyrites-burners enters and meets the nitrous vitriol descending; at the same time either a jet of steam is introduced separately, or the gas is previously conducted through tanks filled with water, in order to be saturated with moisture.

In these apparatus the denitration evidently took place by the joint action of the steam and the sulphurous acid. The acid ought to arrive at the bottom entirely free from nitrogen compounds; but it is so dilute that it can only be run into the chambers. Such apparatus are hardly to be found in use in any place now-a-days, for good reasons. Since the acid is in them diluted to the same extent as in the process of denitrating by hot water or steam alone, they present no advantage over the latter; indeed they were in the first instance replaced by the latter processes. But the apparatus just described have this drawback, that they last a very short time, on account of the rapid destruction of the lead. The destructive action is always very strong in the first chambers, which, even under the best conditions, and in the presence of a Glover tower, suffer more than the remaining chambers, and have to be made of thicker lead if they are to last as long. The reason of this is partly the heat of the gas, partly the nitrous compounds themselves. It is evident how much more of this action must take place in a very small chamber, such as the "shelf apparatus" or Gay-Lussac's "Dénitrificateur." The worst, however, of these apparatus is that the steam introduced into them necessarily leads to the condensation of very dilute sulphuric acid and nitric acid on the sides of the apparatus, which must rapidly corrode the lead. Bode calls attention to another very important circumstance. Considering the small size of the chambers serving as shelf apparatus or dénitrificateurs, any changes in the chamber-process, in the composition of the kiln-gas, of the supply of steam, of the outer temperature, &c. must be felt in them very much more than in a large lead chamber. Therefore, from time to time, stronger nitrous vitriol will condense on the walls, and be diluted directly after by an increased condensation of water, and thus become charged with nitric acid. As every practical man knows, the interior walls of a working lead chamber are always covered with a white slimy lining of lead sulphate, which holds back acid like a sponge, but at the same time protects the lead from further action, until such time as the acid is diluted by condensed steam, gas is given off from it, and the slimy mass of lead-sulphate is loosened and washed off, whereupon the lead is again exposed to fresh attacks. The older denitrating-apparatus, therefore, were doomed to very rapid destruction, because they employed the simultaneous action of sulphurous acid and of steam.

In England, most manufacturers passed over to ***diluting the nitrous vitriol*** in separate small boxes ***with water and steam,*** whilst on the Continent usually "steam columns" or "cascades" were preferred. The English arrangement, such as was almost general up to a few years ago, and which has only been thrown into the background by the Glover tower, is shown in fig. 182. *a* is a lead vessel, about 1 foot high and 18 inches wide, which stands within the lead chamber, very near the inlet for the kiln-gases. Three pipes, *b*, *c*, and *d*, lead into *a*, passing through the side of the chamber and burnt into it. Of these *b* conveys steam, *c* water, and *d* nitrous vitriol; *c* and *d* end in funnels, through which the liquids run. The steam comes from a steam-boiler. The vessel *a* is first filled with water; this is then heated to the boiling-point by steam; and now steam, water, and nitrous vitriol are admitted in such proportions that the latter is completely denitrated before it can run over out of the box *a*. The proximity of the gas coming from the pyrites-burners acts in this way: the escaping oxides of nitrogen are at once spread through the chamber and are mixed with the other gases; and at the same time that gas protects the lead against corrosion.

Fig. 182.

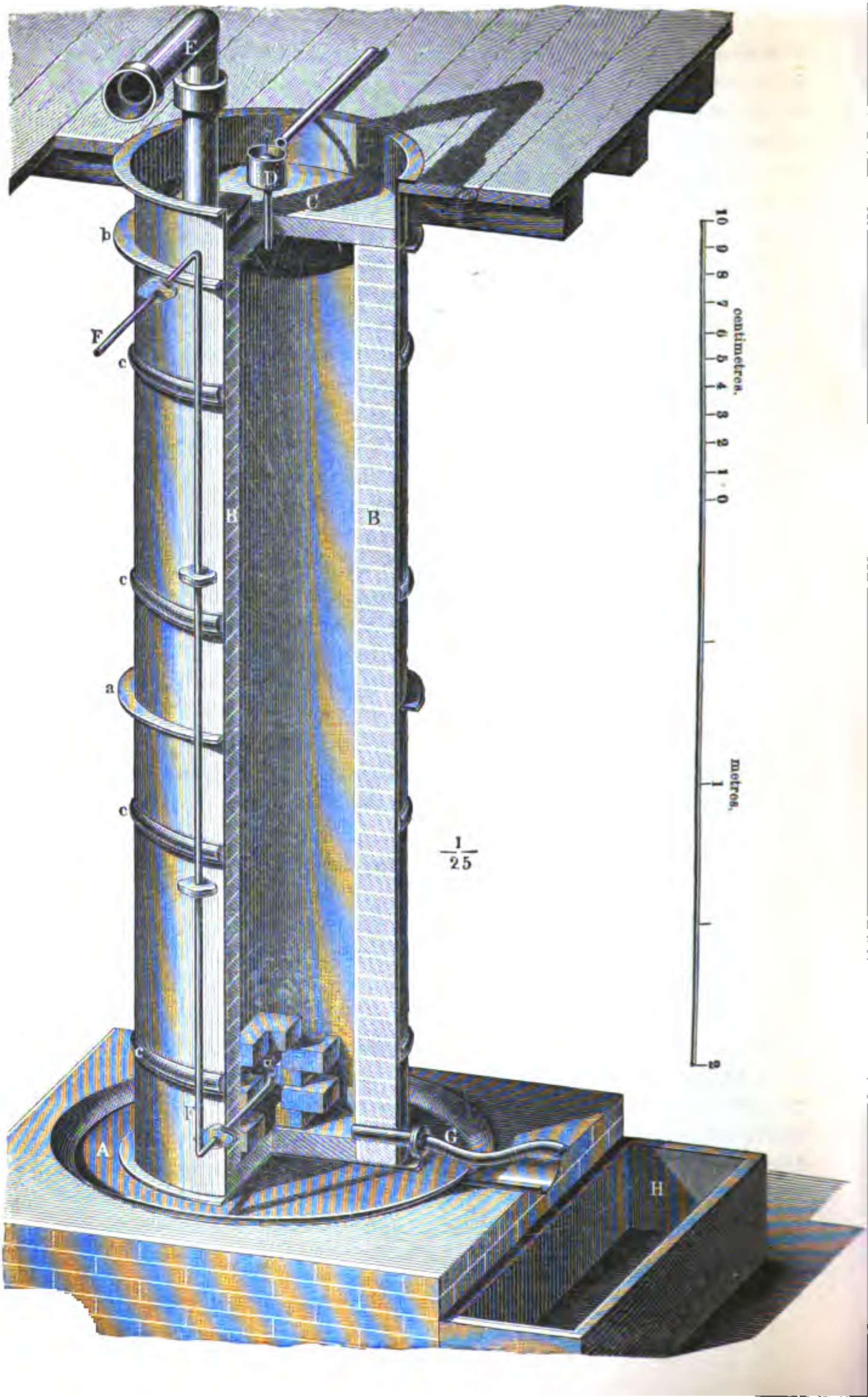


More perfect is the arrangement usual on the Continent, where the denitration takes place on *cascades*, entirely similar to those described previously (p. 309), only with the addition of a contrivance for introducing hot water, which is visible at *a* in fig. 144, on page 315. This is a wrought-iron box, with an outlet-cock, in which water is always kept at the same height by means of a higher tank with a self-acting float-cock, or in any other convenient way. The water in *a* is heated by means of a steam-pipe. It is cheaper to put the waste-cock for the water condensing in all the chamber steam-pipes over the vessel *a*, wherever the levels admit of it; then warm water will be got without any expense. Furthermore, in this case a porcelain dish is set on the top of the cascade, into which the nitrous acid and warm water are poured out, lest through the heat generated in mixing the strong acid and the hot water the material of the cascade itself should suffer. The pot *e* is also here very useful in order to take samples for testing the strength and the degree of denitration of the acid. The latter, when arriving at the bottom, ought to show at most 110°, better, according to Bode, only 100° Tw., to make sure that it is completely denitrated; exactly the same holds good of the steam-columns, to be described directly.

The *denitration by steam alone,* or by steam with very little water, takes place in the so-called *steam-columns,* of which Schwarzenberg has described one of the most usual forms as follows:—

"Fig. 183 represents a steam-column on a scale of 1 : 25. In the diagram a piece of the side is cut out to show the interior of the apparatus. It consists of a cylinder about 11 feet 6 inches high and 3 feet wide, standing on a solid piece of masonry. It is made of strong sheet-lead, and composed of three pieces, whose joints, at *a, b,* are burnt together. The bottom, A, is united to the cylinder in the same way. Four strong iron hoops, *c,* increase its stability. In order to protect the lead against the corrosive action of the hot acids, it is provided with a lining, B, of hard-burnt fire-bricks, which are specially moulded for this, and ground together so as to make a tight joint. The joints are grouted with a mortar made of ground fire-clay. On the top the steam-column is closed tight by means of a slab of fire-clay resting on the brick lining. In the centre of the cover the lead pipe, D, serves for feeding the column with nitrous vitriol. Its funnel is closed with an acid lute. Beside this the stoneware pipe, E, is put tight into the cover, for taking the nitrous acid away into the chamber. Sometimes these pipes are surrounded by a jacket of lead, in order to avoid any interruption of work by their cracking. The steam is introduced into the column through the pipe F, near its bottom, at such a height that the mouth of the steam-pipe remains above the sulphuric acid collecting there. This mouth is covered up and built round with bricks in such a way that proper channels remain for the steam and the acid. On the top of this the column is filled with bits of flint nearly up to its cover; they are about the size of a fist near the bottom, and decrease towards the top to the size of a walnut. In the place of these some works use bits of broken stoneware. The nitrous vitriol running in at the top trickles down through the bits of flint, and is decom-

Fig. 183.


E
D
C
b
F
c
B
B
c
a
c
c
A
F
G
H
1/25
centimetres.
10 9 8 7 6 5 4 3 2 1 0
metres.
1
2

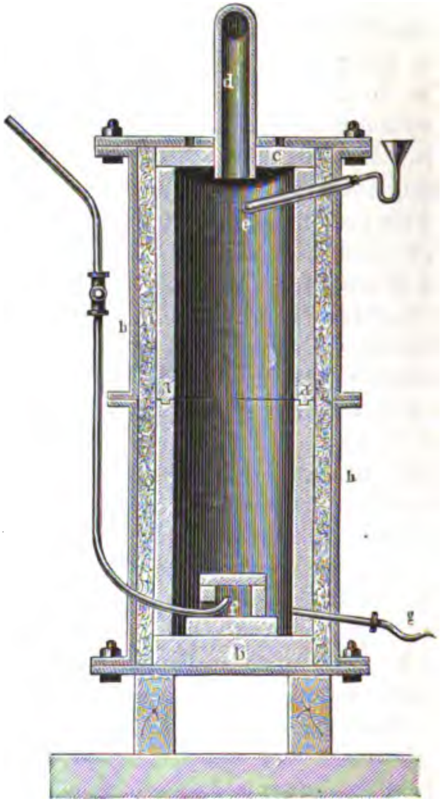
posed in this way by the rising steam. Whilst the nitrous acid given off from it goes away into the chamber through the pipe E in the state of vapour, the sulphuric acid, diluted by the condensed water, arrives at the bottom of the steam-column, and runs through the pipe G into the tank H. The pipe C is so bent as to remain always luted by the acid."

According to Bode, this column, at the Royal Saxon factories at Freiberg, suffices for a system producing 125 cwt. of sulphuric acid of 170° Tw. in 24 hours. He further remarks that the bottom of the cylinder is not joined to the lead saucer A, but stands loose in it. He also says, very justly, that the fire-bricks forming the lining must be boiled in coal-tar, and joined with tar mortar, not with ground fire-clay alone. Such ground fire-clay would not only, as Bode says, be washed out, but it might swell, by the formation of aluminium sulphate, and lift off the cylinder-cover. The tar mortar is made by kneading together finely ground fire-clay with coal-tar, thickened by boiling. It must form a perfectly homogeneous, plastic mass—which is effected on a small scale by beating with a mallet, on a larger scale by grinding under edged runners.

In a large factory near Newcastle there existed, till 1873, steam-columns consisting of a cast-metal pipe 3 feet wide and 9 feet high, with a lining of lead and another lining, inside the first, of thin bricks (2 inches), and a packing of flints. Since then they have been replaced by a Glover-tower steam-columns.

There are also steam-columns made without a lead-jacket; but they cannot then be built up of bricks, but must consist of a single piece. Bode figures such a column, erected by Dr. Gilbert at Hamburg (fig. 184). Its inner diameter is 1 foot 3½ inches, its height 13 feet 1 inch. It consists of two gas-retorts, *a a*, made tight at the joint, after heating the same, by asphalt. The bottom, *b*, and the cover, *c*, are formed of round fireclay-slabs; the latter contains an opening for the stoneware pipe *d* for carrying off the nitre-gas and the excess of steam into the chamber. The nitrous vitriol enters at *e*, the steam at *f*, and the denitrated sulphuric acid runs off at *g*. The retorts are surrounded by the cylinders *h h*, of ½-inch cast iron, which are bolted together and to the cast-iron top- and bottom-plates. A space of 1½ inch remains between the cast iron and fire-clay, and is filled with melted asphalt having a very high fusing-point. The column is filled with bits of flint; the mouth of the steam-pipe is protected by loose bricks. This apparatus has been in operation for five years without giving any trouble, and has supplied a set making 6 tons of acid of 170° Tw. in 24 hours.

Fig. 184.



In other works the steam-columns are made much smaller, which agrees with Bode's views. In Würtz's 'Dictionary of Chemistry,' iii. p. 157, Scheurer-Kestner figures a column made of a piece of lava 6 feet 6 inches high, and only 8 inches wide inside, 2 feet outside, filled with broken glass. Otherwise it offers no peculiarities. The simplest and cheapest for this object are stoneware Woulfe's bottles of about 55 gallons capacity, as shown in figs. 185–187 (after Bode). They are filled with bits of flint. Of the two bottom

Fig. 185.

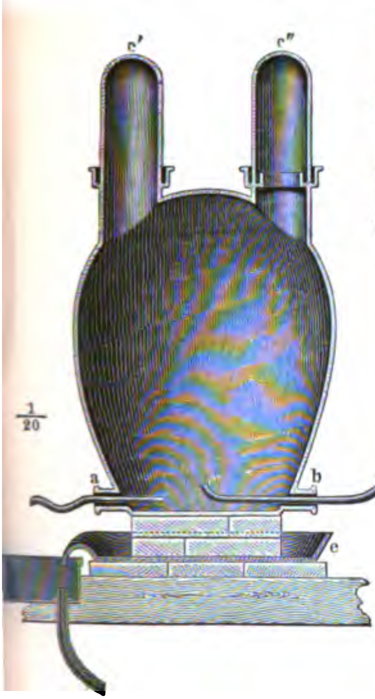


Fig. 186.

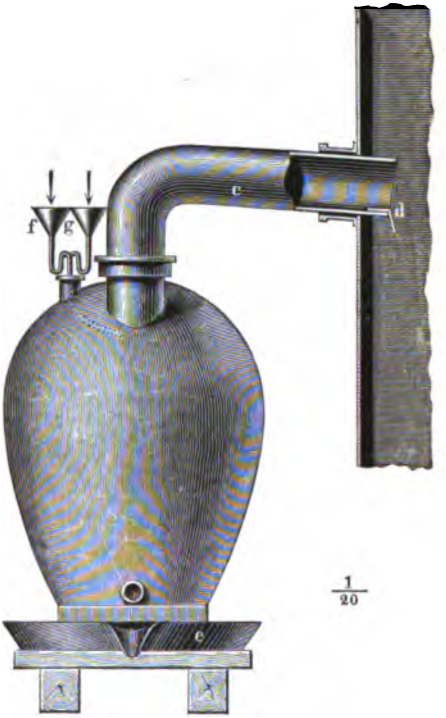
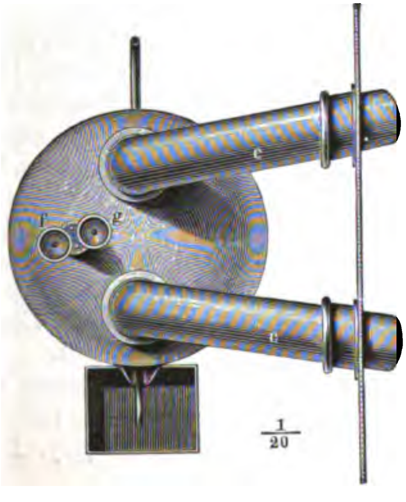


Fig. 187.



branches, *a* and *b*, one serves for running off the dilute acid, the other for the steam-pipe. The nitrous gas escapes through the two pipes *c c*, joined to the jar with cement (like *c'*), or by a hydraulic lute (like *c''*). The pipes *c* are continued into lead pipes having some fall towards the chambers. The jar stands in a stoneware saucer, *e*, on a foundation of fire-bricks; through *f* nitrous vitriol, through *g*, in case of need, water is introduced. If one jar is not found sufficient, a second one can be put up at very little expense.

The first exact comparison between steam-columns and cascades, touching their capacity and expense of working, was made by Bode in his prize essay. His conclusions were as follows:—As to first cost of erection, a complete steam-column is dearest, next to it a cascade; the cheapest are the jars, even if several of them have to be employed. In the steam-columns and the jars the acid can be completely denitrated, so that it will give no reaction with sulphate of iron; with cascades it is not possible to go so far; but, for all that, no more nitre seems to be used with the latter. In the steam-columns the most vulnerable part is the stoneware pipe for taking away the gas; in the cascades, the junction-pipe between the two lead pots. Bode also quotes, as a drawback of the steam-columns, that it is mostly necessary to *pump* the acid out of them into the chambers, because they are mostly placed on the ground. In the factories visited by the author he has always found the columns placed high enough for the acid to run direct out of them into the chambers. If the nitrous acid has to be pumped to the top of the steam-column, this will not be appreciably higher than to the top of the cascades. Bode on the whole prefers the jars, if no Glover tower can be erected; but he makes a condition very difficult of fulfilment, viz. that the jars be of a material capable of resisting the heat. So far as the author's experience goes, he has never seen jars of 55 gallons which could hold out for any length of time against the successive action of cold nitrous acid and of steam; and he would advise any manufacturer not to practise such economy in a matter of very small moment, but to prefer to perishable stoneware jars an everlasting piece of lava or of basalt. The small size mentioned by Scheurer-Kestner is quite sufficient.

The expense of denitrating in steam-columns and cascades has been calculated by Bode (*l. c.* p. 48), so far as this is possible, considering the many circumstances coming into play. But since for these calculations such a number of arbitrary assumptions have to be made that the results cannot be applied to real cases, we will only remark that, according to them, the denitration in steam-columns is dearer than that on cascades, as may be imagined beforehand—the former consuming a great deal of steam, the latter little or none, if hot condensation-water be used. Many manufacturers still prefer the steam-columns to the cascades, as in the former the denitration is much more under control than in the latter, or in the boxes described at p. 414. On the other hand, at the Oker works (*cf* .Bräuning, *l. c.* p. 141) the steam-columns previously erected have been abandoned owing to their continuously breaking down; and they have been replaced in the older sets by cascades, in eight more recent sets by Glover towers. It has been found there that the cascades often yield sulphuric acid containing nitric acid; and therefore a steam-injector has been fixed to the first small chamber, by which the strength of the acid in this chamber is reduced to 110° Tw.

The apparatus which is now used more than all the other denitrating apparatus taken together is the *Glover tower*, which is properly treated in this Chapter, since its inventor had in the first instance constructed it for denitration, although it might just as well be described as a cooling and as a concentrating apparatus. The Glover tower was invented by Mr. John Glover, of Wallsend, near Newcastle-on-Tyne. According to personal information received from Mr. Glover, he had built his first tower already in 1859, at the Washington Chemical Works, near Durham. This tower was made of fire-bricks, and packed with a network of thin fire-tiles. It lasted a year and a half, and proved the correctness of the principle. In 1861 Glover, at the same place, built a lead tower; and when founding another works at Wallsend in the same year, he, of course, built a similar tower there as well, which worked until 1863 or 1864. From the experience gained in this way, Glover constructed in 1864 a third tower, which, in all essential points, was the same as is used to this day. Up to that time only his nearest neighbours had introduced the tower. It must here be observed that its inventor had not only taken out no patent for it, but, with great liberality, showed it to every one interested in the matter. In spite of that, some of the manufacturers on the Tyne, intending to "improve" the tower, committed mistakes in its construction; and, at least in one case, this led to its being given up again, although it has since been reintroduced. Between 1868 and 1870 all the larger and better-managed works on the Tyne introduced the Glover tower; it was adopted in Lancashire about 1868, at London in 1870. Until 1871 nothing had been published about the Glover tower; and it was entirely unknown outside the English alkali-works till the author published a paper on it in 'Dingler's Journal' (vol. cci. p. 341), which made it generally known in Germany, and led to its adoption in that country. The objections raised against the tower as a denitrating apparatus (nobody has ever doubted its excellence as a concentrating and cooling apparatus) have been completely refuted. The first objections raised by Bode ('Dingler's Journal,' ccii. p. 448) were immediately refuted by the author (ib. p. 532), and have since been withdrawn by Bode himself. Bode has become one of the most zealous constructors and advocates of the Glover tower. Also the objections raised by M'Culloch (Chem. News, xxvii. p. 135) have been answered by Glover (ib. p. 152), by the author (ib. p. 162), and Bode (prize essay, p. 5). M'Culloch himself afterwards changed his opinion. Much more serious objections have been made by Kuhlmann (Hofmann's Official Report, i. p. 174) and by Vorster ('Dingler's Journal,' ccxiii. p. 506), on the assumption that the contact of hot sulphurous acid and nitrous vitriol in the tower causes a considerable loss of nitre compounds in the shape of nitrous oxide or of free nitrogen. It is certainly a fact that, under certain conditions, hot sulphurous acid reduces the nitrogen oxides down to nitrous oxide or even to nitrogen. But that such conditions exist in the Glover tower Kuhlmann could not prove, because he had none at his disposal; nor has Vorster experimented with the tower itself in this direction, although he made other interesting observations respecting it; but, entirely on the strength of laboratory experiments, he asserted that 40 to 70 per cent. of the nitrous compounds were lost in the Glover tower. His experiments, however, were made under totally different conditions from those existing in the Glover tower; and the author succeeded in reducing Vorster's inferences on the loss of nitre *ad absurdum* from his own figures ('Dingler's Journal,' ccxv. p. 56, ccxvi. p. 79). In the experiment considered by Vorster the most conclusive, he passed hot sulphurous acid mixed with air for 27 minutes through nitrous vitriol heated to 180° C.; and it is inconceivable how he could assert that this condition answers to that in the Glover tower. Into this the nitrous vitriol enters quite cold, mixed with chamber-acid; and only on leaving, when its heat is greatest, does it attain 130° C. It is out of the question that it should have that temperature in any considerable part of the tower, much less 180°, as in Vorster's experiment. On the contrary, that acid which shows a little higher temperature (but never as high as in Vorster's experiments) contains next to no nitrous acid, but is only further concentrated by hot kiln-gas; and, at all events, the denitration takes place to the greatest extent in the upper part of the tower, where the acid is still pretty cold. This follows with certainty from the well-known fact that the denitration of dilute acid takes place readily, that of concentrated acid with great difficulty. Apart from this, the acid is never exposed to the current of hot sulphurous acid so long as in Vorster's experiments. If once the packing has been quite impregnated, the acid gets from the top to the bottom in a few minutes; but, owing to its fine division, it is almost entirely denitrated near the top. In short, Vorster's experiments must be called worthless for deciding the matter in question, even if they were not refuted by the plain fact, that with the Glover tower the waste of nitre is *at least* no higher than with any other process. More about this below.

The author has lately (Berichte der deutschen chem. Gesellsch. x. p. 1432—more explicitly in 'Dingler's Journal,' 1877, ccxxv. p. 474) criticised in detail the experiments and statements of Kuhlmann and Vorster, and has proved their irrelevancy. He has further proved by experiments that, if the sulphurous acid gas is mixed with a similar excess of oxygen as in the kiln-gas, this mixture decomposes nitrous vitriol, even at a temperature of 200° (in the Glover tower it never gets beyond 130°), in such a way that the *whole* of the nitrogen oxides can be recovered by absorption in concentrated sulphuric acid. Pure sulphur dioxide, free from oxygen, does not act on nitrous vitriol at 110°–130°, but only at 200° C., in such a way as to cause the formation of some nitrous oxide. This, however, is not a practical case at all; and it remains a fact that in the Glover tower neither nitrous oxide nor nitrogen are formed in appreciable quantities. The author's experiments and calculation have been attacked as inexact by Hurter ('Dingler's Journal,' ccxxvii. pp. 465 & 563), but have been completely vindicated by the author (ib. ccxxviii. pp. 70 & 152).

If there were any truth whatever in Kuhlmann's and Vorster's assertions, it would certainly be a cause of still greater loss when the fresh supply of nitre-gas is carried through the tower, as is done in the great majority of English, or when even the liquid nitric acid is run through it, as in many continental works. Then not merely 70 per cent. of the nitrous vitriol, but also 70 per cent. of the fresh supply of nitre, or nitric acid, would be wasted by the tower. This certainly would be felt in a very sensible manner. But in 1871, of the ten works on the river Tyne which possessed Glover towers, only three worked so as to decompose the nitre by the gas of separate pyrites-burners, and to take the gaseous mixture past the Glover tower direct into the chambers. The other seven works sent the gas of *all* burners, along with all the fresh nitre-gas, through the towers, *without consuming any more nitre* than the three former ones. Among these three works was that managed by the author, who, in his first publication, recommended this arrangement. Later on, from experience gathered in the meantime, the plant was altered, and *all* the kiln-gas, along with the nitre-gas, was taken into the Glover tower; but no extra consumption of nitre whatever could be detected. In the same way Mr. Schaffner, of Aussig, found no extra consumption ensue when he began introducing all the liquid nitric acid through the Glover tower.

Glover himself reports (Chem. News, xxvii. p. 152) that he had consumed, for 1651 tons of sulphur (from Norwegian pyrites), only 63 tons 13 cwt. of nitre, =3·8 per cent., with a chamber-space of 20 cubic feet to 1 lb. of sulphur burnt in 24 hours. His pyrites only contained 40 per cent. of sulphur, as the author knows very well, since he used the same quality at that time; the conditions of work were therefore not so favourable as with richer ores. At the same time Glover concentrated all his chamber-acid to 140°–150°; and this is a common experience in most works.

The most important thing is this: it is absolutely certain, from the practical experience of many works, that with the Glover tower rather less nitre (never more) is used than with steam-columns or cascades. This is witnessed, for instance, by the former opponent of the Glover tower, Bode, in 'Dingler's Journal,' ccxvii. p. 305, and in his prize essay, p. 87; and, altogether, no contrary statements of those who have had practical experience of the tower have been given to the world. On the contrary, the Glover tower has not only been generally accepted in England, but also to a great extent on the

Continent, especially in Germany; and the best proof of this is, that in 1875 the Berlin Society for the Promotion of Industry offered a prize for an essay on this subject, in which the utility of the Glover tower for most cases is expressly presupposed, and only its applicability for kiln-gas of inferior heat is mentioned as doubtful and requiring examination. The result of this was Bode's often-mentioned essay on the Glover tower. Now-a-days the Glover tower forms an essential part of every well-arranged sulphuric-acid works, and holds the same rank with the Gay-Lussac tower. Certainly it will not answer to the expectations when constructed in an improper way or from unsuitable material, and therefore, at first, was here and there demolished again; but the same thing must be said of every apparatus used, in the whole range of industry; and the *consensus* of the great majority of manufacturers has entirely decided *for* the Glover tower. Bräuning (*l. c.* p. 140) also quotes the experience of a whole series of works at Oker in which the tower is employed, and where, since its introduction, less nitre is used than before, in consequence of the acid being completely denitrated, so that no loss can be incurred through the reduction of nitric acid to nitrogen or nitrous oxide. On an extensive tour through a number of the best English, German, and French alkali-works, the author has everywhere received the same information, viz. that since the introduction of the Glover tower less acid is consumed than formerly (with the diluting process). This may very frequently be in consequence of the chamber-acid being also denitrated in the Glover tower; but in some works the acid of the large (or first) chamber is not kept nitrous at all, and in others, from various causes, only a small portion of the chamber-acid passes through the Glover tower. In no case is there the slightest reason for asserting that the Glover tower, by itself, wastes more nitre than the diluting process. At Malétra's works at Rouen, before the introduction of the Glover tower, 2 parts, after it only 1·3 part of nitre has been used to 100 parts of pyrites.

It must not remain unmentioned that Cl. A. Winkler, in 1867 (*l. c.* p. 24), proposed very clearly the denitration of nitrous vitriol by sulphurous acid, without having any knowledge whatever of the fact that this plan had been carried out for some years in practice by Glover and others. Moreover Winkler's plan was vitiated by his proposal to add a small quantity of water. He evidently had no idea of the concentrating action of the apparatus which is now called the Glover tower.

Description of the Glover tower.—This in many respects resembles the Gay-Lussac tower, but in others is quite different; and its function is exactly the opposite of that of the Gay-Lussac tower—viz. to deprive the nitrous vitriol running off *at the bottom* of the Gay-Lussac tower of its nitrous compounds, and to restore it to a proper state of concentration for applying it again *at the top* of that tower. This, certainly, is only one of the functions of the Glover tower, but the most important and characteristic of all. The tower fulfils this function by exposing the nitrous vitriol, usually mixed with chamber-acid, in a finely divided form, to the action of the hot burner-gas, whose heat acts concentratingly upon the sulphuric acid, and whose sulphurous acid acts denitratingly upon the nitrosulphonic acid; and the simultaneous concentration and action of the sulphurous acid seem very much to advance the denitration. Glover's apparatus cannot be put in the same line with the apparatus described above (p. 412), because in it no condensation of dilute vitriol containing nitric acid can take place on the lead walls, and because it is altogether so constructed that the lead nowhere comes into contact with the hot gas and the nitrous vitriol. Once properly built, it goes on working for many years, and causes no interruption of the process. Besides, it possesses two very great advantages. The first is, that it is both the most complete and the most rational of all cooling-contrivances for the burner-gas:—the most complete, because the gas is brought into immediate contact with the cooling-liquid in the shape of a fine spray, not separated from it by a metallic wall or only exposed to the cooling action at the circumference of the current; the most rational, because no expense has to be incurred for pumping up cold water for cooling, but the generated steam is at once usefully employed in the chamber. The second and still greater advantage of the Glover tower is that in it not only all the acid serving for absorption in the Gay-Lussac tower, but the whole of the chamber-acid is brought to 152° Tw. without any expense except that of pumping the acid to the top of the tower—an expense which is very small indeed, especially in the case mentioned on p. 393, where the exhaust-steam of the air-pumping engine is used as steam for the chambers.

The Glover tower is, moreover, now used for introducing the requisite fresh nitric acid, or a solution of nitrate of soda, into the chambers without any special apparatus, by running it down along with the nitrous vitriol. Before it arrives at the bottom it is fully denitrated, as well as the nitrous vitriol itself.

The Glover tower may also operate with only the nitrous vitriol itself running down in it, without any chamber-acid; but in that case it does not deprive it of all the nitrous compounds, but of the principal part only (down to about 0·2 per cent. of N_2O_3), and at the same time concentrates it to 152° Tw. This acid may now be used again in the Gay-Lussac tower for absorption; and thus a circulation of acid may take place between the two towers. There is in this always a little addition to the acid, as within the Glover tower itself, by the action of the sulphur dioxide on the nitrosulphonic acid, free sulphuric acid is formed.

$$2SO_2(OH)(NO_2)+SO_2+2H_2O=3SO_2(OH)_2+2NO.$$

This equation represents the essential reaction going on in the Glover tower.

However, the Glover tower is not usually fed (in the way just mentioned) with nitrous vitriol alone, but only in the case of temporary disturbances. The apparatus is always so arranged as to be fed with nitrous vitriol (or with fresh nitric acid) and chamber-acid *together*, in which case not only is the denitration completed, owing to the initial dilution, but the acceptable secondary effect is obtained of concentrating the chamber-acid up to 152° Tw., and of depriving it also of the minute proportion of nitre which it generally contains. If the acid is not, as is usually assumed here, brought in the chambers themselves to 116°–124°, but only to 106° Tw., it can for all that be concentrated to 144° without any difficulty in the Glover tower, even when the gas comes from a shelf burner for pyrites smalls and has therefore to be somewhat cooled in dust-chambers, on the supposition that the tower is placed close to the burners. This is done, for instance, at the Aussig works in Bohemia. That the denitration by sulphurous acid becomes more perfect by dilution, is a matter of course, according to the above-quoted researches of R. Weber and Cl. Winkler (*suprà*, p. 370).

The stream of nitrous vitriol and that of chamber-acid are regulated entirely according to the degree of denitration and of concentration shown by the acid running off at the bottom of the Glover tower. The more chamber-acid is run through (that is to say, the greater the dilution), the easier will be a full denitration; the less chamber-acid is used, the more concentrated will the acid arrive below. There is, however, no difficulty in attaining *both* objects, viz. to get an acid at the same time completely denitrated and showing 152° Tw., if good pyrites (with 42 per cent. and upwards of sulphur) be burnt, and if the burner-gas be employed as hot as possible, say 300° C. and upwards, by placing the tower close to the burners. In the case of poor ores, or of smalls-burners with large dust-chambers, the denitrating action will also be complete; but the concentration cannot then be carried so far.

If it be assumed that the Gay-Lussac tower receives a quantity of acid equal to the total daily production (and this, indeed, satisfies all requirements), there will, of course, be just the same quantity of SO_4H_2 running down the Glover tower in the shape of chamber-acid, along with the nitrous vitriol, and therefore, according to bulk and weight, a little more of the chamber-acid, as this is more diluted. If the chamber-acid is on an average $=123°$ Tw., equal to 70 per cent. SO_4H_2 (it may be safely brought up to this strength, precisely because the nitre dissolved in chamber-acid, when rather strong, will be expelled and utilized in the Glover tower), 117 parts by weight of the same correspond to 100 parts by weight of an acid of 152° Tw., $=81·7$ per cent. SO_4H_2; or 100 vols. of the latter are equal to 128 vols. of the 123° acid, and the latter would be the proportion in which the two acids are mixed. The result would be a mixture of acids of 136° Tw. entering the Glover tower at the top, which can be fully denitrated by sulphurous acid, especially when hot (Weber, *suprà*, p. 370). If less Gay-Lussac acid has been used than the above, the mixture of acids entering the Glover tower will show a lower specific gravity than 136° Tw., and will be all the more easily denitrated.

During the first years of the working of the Glover tower it was generally assumed that the acids must only be mixed *inside the tower*, because during their mixture nitric oxide would be given off. On this principle was founded the mixing-apparatus described by the author in his first publication on the Glover tower (in Dingler's Journal, cci. p. 348), and the distributing wheels with double outlet and separate distributing chambers and pipes. But it follows from the calculation just made that a mixture of equal parts of acids, when chamber-acid of 123° Tw. is used and the daily make of acid is passed through the Gay-Lussac tower once a day, would be equal to 136° Tw. In an acid of this strength nitrosulphonic acid is entirely stable, at least at the ordinary temperature; and it is possible, and has been done in many places for years past, to mix the two acids before they enter the Glover tower, which greatly simplifies the distributing apparatus. Even when only one half of the total daily make of acid is used for absorbing, the mixture of this with the total chamber-acid still comes to 131° Tw., which is equally a safe strength. If, however, the conditions are the most unfavourable in this respect, the dilution can no longer take place outside the tower. If, for instance, the chamber-acid is only 106° Tw. strong, 131 parts by weight of it correspond to 100 parts of acid of 152°; and if of the latter only half the equivalent is taken (that is to say, 100 parts by weight of acid of 152° Tw. to 262 parts of 106°), the density of the mixture only comes to 118°, at which strength nitric oxide begins to escape from a solution pretty rich in nitrosulphonic acid.

In these calculations the degree of saturation of the vitriol with nitrous compounds is not yet taken into account; the less the amount of acid used every day in the Gay-Lussac tower, the more will it be saturated with nitre, and there will be more danger of gas escaping from the nitrous vitriol when mixing it with chamber-acid.

The temperature of the acid running off from the Glover tower is usually between 120° and 130° C. If the work is very much pushed, it may reach 140° or even 150°. In the few works where this happens, no bad consequences have been observed; but in one works the author was told that a little more nitre was always used whenever the acid became hotter than 138° C. Still the observations made there were not sufficient to establish this result as certain, if all disturbing conditions be eliminated. The gas leaving the tower at the top has generally a temperature of from 50° to 80° C.; it should not be above 60°, at which temperature cooling it before it enters the chambers is quite unnecessary.

The following is a description of a Glover tower erected by the author in 1873, which served for a chamber-space of about 160,000 cubic feet and a daily consumption of 9 tons of 48-per-cent. pyrites. The following diagrams and descriptions are, of course, only meant to serve as an instance of a tower that worked well, but do not

Fig. 188.

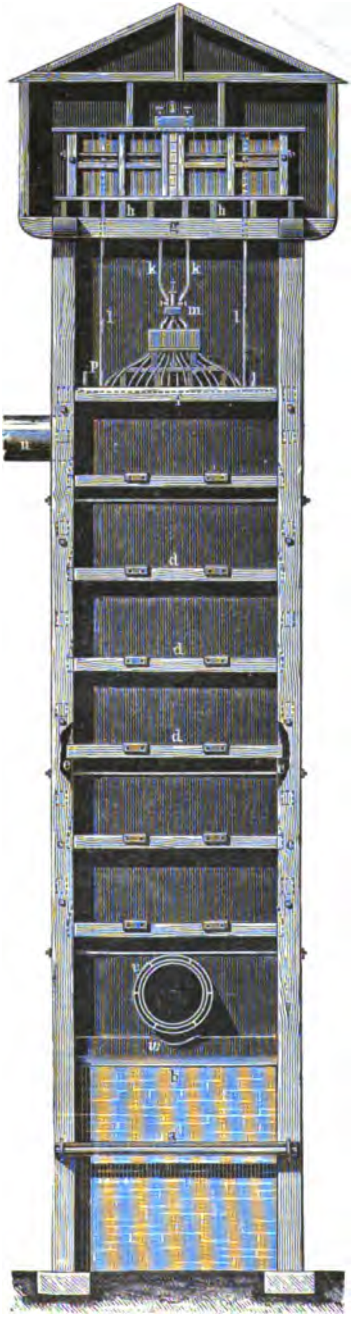


Fig. 189.

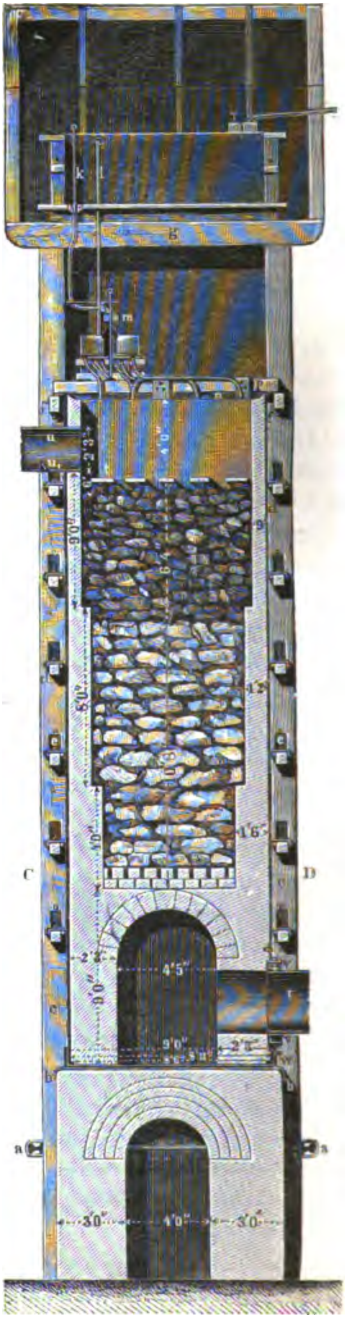


Fig. 190.

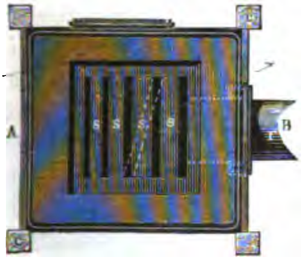


Fig. 191.

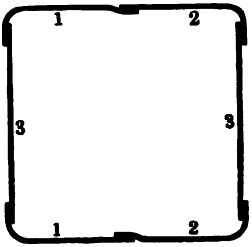


Fig. 192.

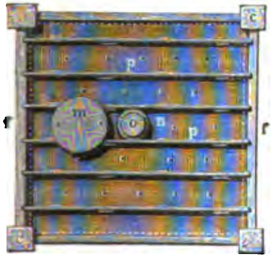


Fig. 193.

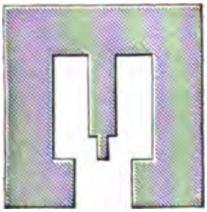
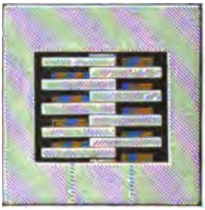


Fig. 194.



claim to be authoritative in all details. Fig. 188 is a front elevation; fig. 189, a sectional elevation through the line AB (fig. 190); fig. 190, a sectional plan through CD (fig. 189); fig. 191, a section through the frame, in order to show the way in which the lead is attached to it; fig. 192, a view from the top, showing the acid-distributor and the man-hole. Figs. 193 & 194 are sectional plans, showing a different arrangement for a grating, viz. fig. 193 below, and fig. 194 above the same. The foundation consists of two pillars of ordinary good brickwork, joined by a fourfold arch and braced together by railway-rails and tie-rods *a a*. It is covered with a lead apron, *b*, of 7 lb. to the square foot, the sole object of which is to secure that in case of leakage of the tower-bottom the acid cannot get to the brickwork, but must run off sideways. Instead of turning this apron down, it can be turned up in the shape of a saucer with a spout. The tower itself is erected within a strong frame of pitch-pine, which at the same time carries the necessary tanks. Four pillars, *c c*, 12 inches square, which are with advantage placed on stoneware slabs to protect their feet from being corroded by acid running over, are joined together by joists

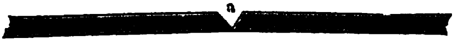
6 inches square, mortised in such a way that they can be knocked out upwards when they have got damaged, whilst the weight of the lead otherwise pulls them downwards. To effect this, the mortise-holes in the uprights are continued upwards in a slanting direction; figs. 188 & 189 show this clearly at *e e*. At the top of the tower stronger joists, *ff*, 6 × 9 in., run all round; these have to support a greater weight. Instead of this kind of frame, the ordinary frame with diagonal stays can be employed; in this case the whole weight of the lead must be carried by the top joists, because the lower joists are missing. At the top the uprights are tied together by the crown-trees *g g* (12 × 12 in.); on these a wooden cabin is erected, within which the acid-tanks are placed. There is, properly speaking, only one tank, which is divided into two by a partition; it stands on the joists *h h*; and its wood construction can easily be seen from the figure. Both compartments are lined inside with lead of 7 lb. to the square foot; one of them receives nitrous vitriol, the other chamber-acid by the distributing-box *i* (details in figs. 196 & 197), to which the acid is conveyed from the delivery-pipe of the higher Gay-Lussac tower, either by means of a special splashing-apparatus (as in fig. 172), or, omitting the box *i*, from a distributing-box with 3 plug-valves, common to them and to the Gay-Lussac tower (as in fig. 173). The latter is the proper thing when both towers are placed side by side, and when their tanks are covered by the same wooden house, which is by far the best arrangement; in that case the tops of the two towers are placed at the same level; but the foundations of the Glover must be made much higher than those of the Gay-Lussac tower, on account of its smaller height. This is far from a disadvantage, as the Glover tower must anyhow be placed at such a height that the burner-gas will have to rise a little in passing to it.

The acid-tanks are each provided with an outlet-valve *k* and a waste-pipe *l*; the former leads to the acid-distributor, the latter direct to the tower-cover *n*. This cover is, as seen best in fig. 189, suspended from joists *pp*, which lie across the beams *ff*; strong straps, nailed to both sides of the joists alternately (figs. 189 & 192), hold the cover fast. This (precisely like a chamber-top, on the edges, where it is burnt to the chamber-sides) is jammed between the beams *f* and joists *p*; but thence towards the centre it is dished out, so that any acid running onto it cannot run down the sides of the tower, but stands in the depression of the cover and runs into the interior of the tower through the hydraulic joint of the man-hole, or through a small swan-neck pipe provided on purpose.

The *tower itself* is made of 14-lb. lead, its bottom of 35-lb. lead, the straps of 9-lb. lead. Its sides are suspended from the top and side joists, just like those of a chamber. Figs. 189 & 191 show clearly that the lead stands a little off the wood, which is of importance for the protection of both the wood and the lead. At the same time figure 191 shows how the sides are constructed. In order to avoid seams at the corners, where they would be weakest and where they could not be very well repaired on account of the uprights *c c*, two of the sides are made of two sheets of lead (1, 2) each, which are burnt together in the middle, and which reach round the corners, where the sheets 3 are burnt to them. All the side sheets reach down from the top to the bottom without any horizontal seams, and hang loosely within the saucer. The tower proper is 30 feet high and has a horizontal section of 9 feet by 9.

The bottom saucer is formed of two sheets of lead burnt together in the middle and turned up all round to a height of 12 inches. Since sheets of 35 lb. to the square foot cannot be burnt together in the usual manner, they are joined thus: they are placed close together, after having the edges cut off slantingly and scraped clean (fig. 195); into the rebate, *a*, thus formed, lead heated a good deal beyond its melting-point is poured; the latter, before solidifying itself, fuses the margins of *a*; and this is further assisted by a red-hot iron, so that the whole unites into a solid mass.

Fig. 195.



In England the frame and the towers themselves have latterly been made more and more substantial; for instance, towers are met with whose sides, up to the height of the gas-pipe, are of 25- to 30-lb. lead, and whose saucer is of 50- to 60-lb. lead.

The tower is now *lined* and at the same time provided with a *grating* (dome) for the packing. The lining must consist of the best hard-burnt, acid-resisting fire-bricks that can be procured. Some bricks are not quite so suitable as others; for instance, the "blue" bricks of Mold, in Flintshire, are better adapted for this purpose than other bricks of a more refractory but less acid-resisting nature. Best of all, but more expensive, are bricks of stoneware or glass. The Aussig chemical works and the Bendorf works near Coblence likewise make very good lining-bricks for Glover towers. The lining is made 2 feet 3 inches thick at the bottom all round, as high as the grating, so that a clear space of 4 feet 5 inches remains open in the centre; the 1 inch remaining from a total section of 9 feet square is caused by not putting the lining close to the lead sides, but leaving a clear space of ½ inch all round (see fig. 190). Immediately over the entrance-pipe *r* for the gas there are four semicircular arches, *s s*, as seen in fig. 189 in section, in fig. 190 from above. They are arched from the side lining, made so strong for this very purpose, and serve both for carrying the lining and for dividing the current of gas. To avoid the side-pressure altogether, some manufacturers, instead of arches, construct a grating of fire-clay slabs, as shown in figs. 193 & 194; the former shows how a dwarf wall runs almost through the middle of the tower-bottom, carrying on its top (fig. 194) a number of slabs standing edgewise, 3 feet 3 inches long by 18 inches height and 6 inches thickness, which rest on this dwarf wall and upon the side walls. In any case the arches, if such are used, are levelled up to a plane surface at the top (fig. 189). The lining of the tower is now continued for a height of about 4 feet with a thickness of 18 inches, then for 8 feet with only 14 inches, and for the last 8 feet with only 9 inches thickness.

The whole lining of the tower as well as the dome (arch) must be walled *dry*, without any mortar of any kind. Tar mortar would melt; and fire-clay would be converted into aluminium sulphate. This happened to one of the first works on the Tyne at which the Glover tower was tried, where after a few weeks the lining lifted up the cover and rose above the tower. In order to make the arch sufficiently stable without any mortar, it should not be made of ordinary fire-bricks cut to shape, but of large fire-clay lumps expressly manufactured for the purpose, whose sides join smoothly together. In some works all the bricks of the lining are ground upon one another, so that only extremely small joints remain.

The *packing* consists of flints which have been purified by hydrochloric acid from all soluble impurities, such as adhering chalk, or of any other acid-resisting and not disintegrating material; in one case the author found stoneware seltzer-water bottles with their bottoms knocked out. The upper third may be made of the hardest and best picked coke, because here the heat is no longer considerable, and the acid is not yet too concentrated. Unless, however, a description of coke can be obtained that really fully resists the acid, it must decidedly be left out; for it will soon became rotten, the pieces will be disintegrated, and the draught will be stopped. There are also instances of the coke having taken fire when the Glover tower was going empty, which sometimes cannot be avoided. Just over the dome, in order to divide the current of gas in a regular way, first two courses of the same kind of bricks as serve for the lining are placed pigeonholewise. On the very top a few small slabs, *t*, are laid down, which cause the acid running in to splash about before reaching the coke. It is a matter of course that the packing must be done as systematically and carefully as that of the Gay-Lussac tower.

In some cases it is preferred not to fill the tower to its very top, viz. if the gas is cooled too much; for then even a part of the first-formed aqueous vapour might be condensed again to the liquid state, dilution thus counteracting the concentration. The temperature of the outgoing gas ought in no case to be below 60° C.; some manufacturers prefer from 60° to 75° C. But if too much cooling must be avoided by leaving the upper portion of the tower empty, that portion might be left out altogether and the tower might be made so much lower. In fact, at some works in England towers of from 18 to 20 feet height are are preferred to higher ones. This will, of course, depend upon the heat which the gas possesses when entering the tower, therefore upon the kind of ore burnt, upon the presence of dust-chambers, upon the length of way from the pyrites-burners to the tower, and so forth. According to numerous notes taken on this subject, the proper height for a Glover tower, under ordinary circumstances, seems to be from 26 to 30 feet.

The *gas* enters through the cast-iron pipe *r*, 2 feet 6 inches wide, and leaves the tower through the lead pipe *u*, 2 feet 3 inches wide. About the latter nothing need be said, except that on its bottom a small ledge u_1 is formed, which compels the acid squirted into it to run back into the tower; this pipe also usually rises a little towards the chamber. On the other hand, the fixing of the entrance-pipe *r*, which ought to have a little fall towards the tower, is not quite such a simple matter, and at first caused much difficulty. It is mostly made of cast iron, and has therefore in the great majority of acid-works, except in the above-mentioned cases, a temperature of at least 300° C. The lead of the tower, where it touches the cast iron, will therefore be quickly wasted, and any kind of cement put between the two will not do much good; in most works a little gas was seen escaping at this joint, and it gave occasion for many repairs. The arrangement drawn in the diagram obviates this drawback. The pipe *r* here is not at all in contact with the lead, but with a metal casting, *v*. The latter is in the shape of a ring with two flanges perpendicular to the plane of the ring; the thickness of the metal is 1 inch, the clear space between the flanges 4 inches, the total height 8 inches, the inner diameter of the ring 2 feet 9½ inches. Since the outside diameter of the pipe *r* is 2 feet 7½ inches, there is a caulking-joint of 1 inch left free all round, which can be filled up with any hard cement—for instance, the ordinary rust cement made of iron filings, sulphur, and sal ammoniac; this cement can be rammed in hard, as it lies between two iron surfaces. In the side of the tower, in the place in question, there is a circular hole to whose circumference an upstanding flange is burnt, fitting the outer circumference of the ring *v*; between the lead and the iron a little ordinary tar and fire-clay cement is put; and a wrought-iron hoop in two parts with screw joints firmly binds together lead, cement, and cast iron. Since the outer part of *v* is cooled by the air circulating in the hollow space of the ring, only a small part of the heat can be communicated to it, which the inner part of the ring receives (already weakened by the layer of cement) from the pipe *r*; and therefore no difficulty is experienced in keeping the joint between lead and iron tight.

At the Aussig works the difficulty is obviated by attaching to the cast-iron gas-pipe coming from the burners a short piece of fire-clay pipe with a flange joint; the latter projects into the Glover tower; and the lead side of this is simply joined to the fire-clay pipe by a burnt-on flange surrounding the pipe, with tar cement between, and with an iron hoop pressing the lead flange onto the pipe. As the fire-clay pipe has much thicker walls, and is a so much worse conductor for heat than a cast-iron one, this joint keeps tight even without the air-cooling just described.

Lastly, we must notice the "lip" *w*, where the lead side of the saucer is turned over to form a place for the acid to run off continually into a leaden spout. This part, over which hot acid is incessantly running, and which cannot remain covered by a protecting layer of lead sulphate, is exposed to very great wear and tear; and as it cannot well be repaired while the tower is at work, the plumber must not neglect to put a false lip, consisting of a piece of sheet lead beaten down close upon the real lip. The acid will then run over the false lip; and the latter, when worn out, can be replaced by a fresh piece in a few minutes' time.

Instead of a "lip," a lead tube of about 1¼ inch bore can be burnt in the side of the saucer, a little below its upper edge; but the plumber must do this with the utmost care, and make the joint extremely strong, in order to save repairs, which can only be done by stopping the work. At Stolberg, where the Glover tower has no saucer, but the bottom and the sides are in one piece, there are two running-off pipes provided, so that one can work when the other is stopped up, &c.

For the *distribution of the acid*, nearly everywhere reaction-wheels are used. They can be constructed as originally designed by Schaffner (p. 386); in England, however, they are usually made almost altogether of lead: this construction is shown on a larger scale in figs. 196 and 197. On a small wooden frame is a cast-iron plate, *a*, perforated with holes in the centre and in twenty-four places not far from the circumference. It serves as a support for a lead cylinder *b*, of 2 feet 6 inches width and 12 inches height, whose bottom is divided into twenty-four compartments by radial ledges 1½ inch high; in each of them there is a hole corresponding to one in the cast-iron plate; and lead tubes, *o o*, of ¾ inch bore, burnt to the lead of the cylinder, are carried thence to the tower-cover, where the pipes are put loosely into short branches burnt to the cover, the joint being made with tar cement; figures 188 and 192 show the way in which the pipes are distributed. In the middle of the cylinder *b* (fig. 196) a smaller cylinder, *c* (7

Fig. 196.

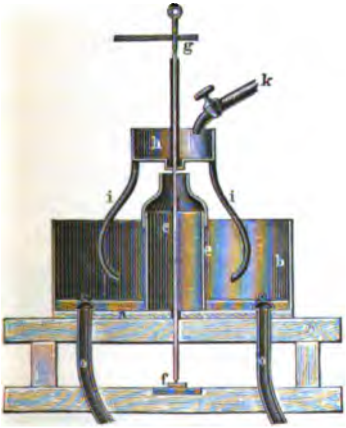
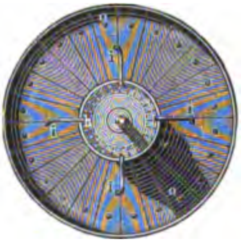


Fig. 197.



inches wide), is burnt on, whose top is covered with a loose cap, contracted in the centre. All these parts are fast. The movable parts consist, first, of an iron spindle, *e*, passing through the cast-metal plate *a*, and resting below with its steeled point on a piece of plate glass, *f*; on the top it is guided by an iron point screwed into an iron support, *g*; by turning the screw the spindle *e* can be made faster or looser. The upper part of *e* is surrounded by a thin lead tube; and at this part a dish, *h*, of thin lead is burnt on, from which the four tubes *i i* descend in the curve shown in both figures, so that the acid from the pipe *k*, when running out of *i i*, causes, by the reaction, the spindle *e* to rotate in the opposite direction, along with the parts fixed to it. Both acids, the nitrous vitriol and the chamber-acid, run into the lead dish *h*. The gas is prevented from escaping by small caps put on the mouths of the pipes *o o*, or in any other way. Exactly the same apparatus is used in the English works for the Gay-Lussac towers.

A contrivance for producing a constant flow of acid, such as we have recommended for the Gay-Lussac tower (see p. 391), is very rarely used for the Glover tower, simply because the quantities of both acids must be regulated by hand in order to get properly concentrated and denitrated acid at the bottom; and this, again, depends to such an extent upon the variable percentage of nitrogen compounds in the nitrous vitriol, that a constantly equal supply, such as that for the Gay-Lussac tower, cannot be carried out.

Through the kindness of Mr. Schaffner the author is enabled to give diagrams of the distributing-apparatus at present working the Glover towers at the Aussig works, in figs. 198 and 199; the reac-

Fig. 198.

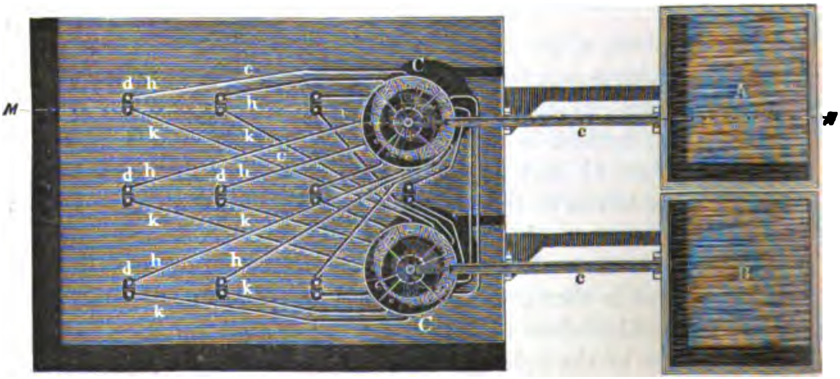


Fig. 199.

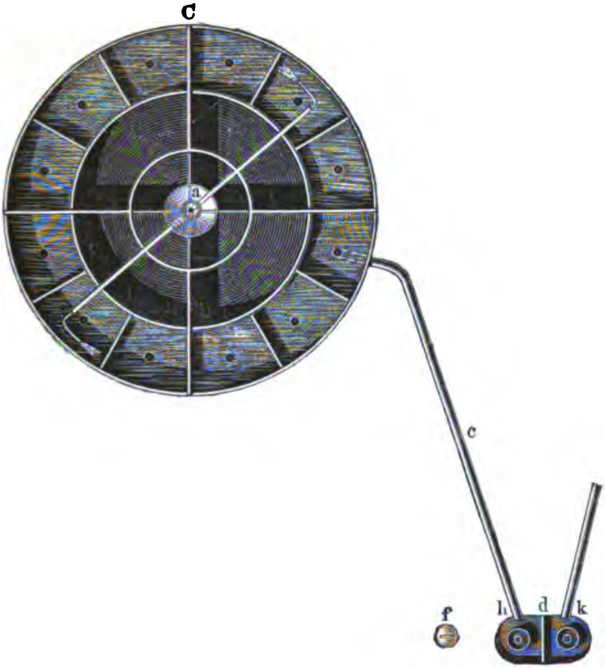


Fig. 200.

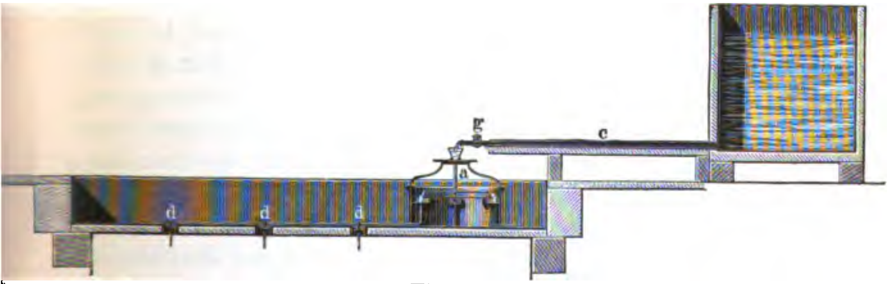
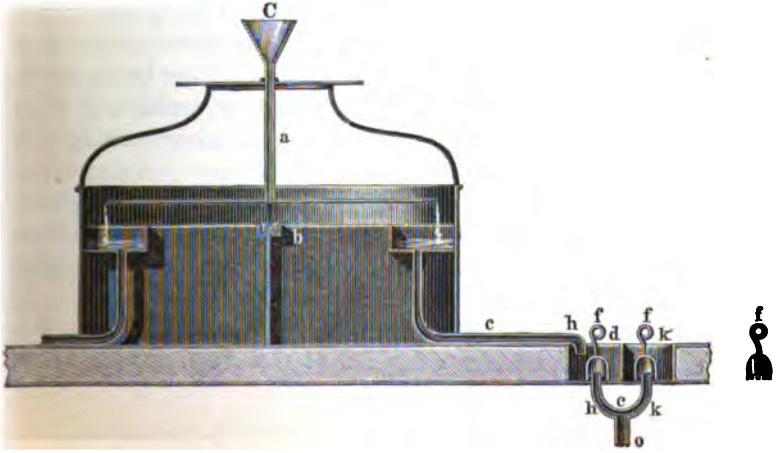


Fig. 201.



tion-wheel is shown on a larger scale in figs. 200 and 201. There are here two reaction-wheels, which in most cases is not necessary. A is the tank for nitrous vitriol, B that for chamber-acid, C the distributing apparatus, *a* the reaction-wheel, *b* the pan on which the spindle revolves, made of hard-burnt fire-clay, *c* lead tubes, *d* supply to the tower (with hydraulic joints—*h* for the Gay-Lussac acid, *k* for the chamber-acid), *f* luting-cup, *g* stoneware cock, *o* the common opening into the Glover tower.

According to the dimensions given above, it is seen that the *cubic contents of the Glover tower*, measured inside the lead, without taking any account of the lining, the space underneath the dome, &c., for a daily consumption of 9 tons pyrites with 48 per cent. sulphur, amounts to 9 × 9 × 30 feet—that is, to 2430 cubic feet. This for every ton of sulphur put in daily amounts to about 550 cubic feet; and this number may be considered the proper one for the proportions of a Glover tower; and at some of the largest works it is closely approached.

Another Glover tower erected by Bode has been described and figured in detail by himself (prize essay, p. 60, Dingler's Journal, ccxxiii. 623); as in principle it offers no deviation from the above-described tower, only those matters will be mentioned in which there are divergencies in detail. His tower is 7 feet 6 inches square and 25 feet high. The packing consists of broken pottery and, at the very top, of a little coke. For the acids there are sixteen inlet-pipes with two reaction-wheels. Bode (*l. c.*) also describes a floating reaction-wheel for very small pressure, which certainly is very perishable, being made of glass. He also describes a special contrivance for mixing the nitrous vitriol and the chamber-acid, which are supplied separately to the two reaction-wheels, immediately after their entrance into the tower. Two branch pipes enter into a common hydraulic lute; and from these a bent pipe goes into the tower, which at the lowest part of the bend, where the two acids meet, has an outlet-hole. Such precautions, in most cases, are quite unnecessary; the acids can be mixed outside (see p. 429).

Some Glover towers are cylindrical (instead of square), with polygonally built-up packing. Instead of a timber frame, such as is described above, in some places a cast-iron or even a wrought-iron frame has been employed with great advantage.

Bode's Glover tower served for a set of "pebble" kilns, between which and the tower a large dust-chamber had been built.

The gas, therefore, only reached the tower 152° to 180° C. hot; and the temperature on leaving it varied between 30° and 40° C. The hot acid running off showed between 96° and 110° C. When this tower was only employed for concentrating chamber-acid, it daily evaporated 6 tons of water and produced 2 tons 3½ cwt. acid of 144° Tw. from chamber-acid of 110°. This corresponds to a saving of coals for chamber-steam equal to 1½ cwt. per diem. When the tower was employed both for concentrating and denitrating, it supplied daily on an average 2 tons of acid of 144° Tw., and evaporated 9 cwt. of water; the denitration was perfect. The kiln-gas had 7½ per cent. by volume of sulphur dioxide. Of course the above results are much less favourable than with the usual initial temperature of 300° to 400° C. Even in the latter case the temperature of the gas leaving the tower does not exceed 50° to 60° C. Such a hotter tower of 8·28 square metres section, according to Vorster (Dingl. Journ. ccxiii. p. 411), in twenty-four hours evaporated 1400 kilog. water; another tower of 4·55 square metres section, 1048 kilog. water, the kiln-gas containing 8 per cent. by volume of sulphurous acid.

According to Wunderlich (Zeitschr. f. d. chemische Grossgewerbe, i. p. 74) and Bräuning (*l. c.* p. 140), Glover towers do not seem to offer any advantage when the temperature at the kiln-gas on entering is below 200° C.; this is the experience of the Oker smelting-works. There each Glover tower, 5 feet 8 inches square and 17 feet 3 inches high, concentrates daily 6 tons 2 cwt. of acid to 144° Tw., but only when pyrites is used; with lead matt and the like the initial temperature of the gas sinks to 230°, and the quantity of acid concentrated to 3 tons of 144° Tw.

Even when in Bode's Glover tower, by an accident, the percentage of the kiln-gas had sunk down to 6 or 5 per cent. of sulphur dioxide, there was still complete denitration and an evaporation of 7 cwt. of water daily, equal to 1·7 ton of acid of 144° Tw. Bode calculates from this that, even when calcining the poorest ores, the Glover tower still remains a useful apparatus.

Hasenclever reports (Ber. d. deutsch. chem. Gesellsch. 1872, p. 506) that the Glover tower had been successful in combination with his plate-burners; the author has found the same in combination with so-called Malétra's or shelf burners in a large number of works, at all of which, of course, there were dust-chambers.

There are certainly two *drawbacks* connected with the Glover tower, one of which is temporary, the other permanent. The coke used for packing the Gay-Lussac tower, and partly also the Glover tower, communicates to the acid, especially at the beginning, a brown colour (due to organic substances), which is quite immaterial to its technical application, but injures its sale. After a little time this ceases; and the acid running away from the Glover tower is then as clear as water, and, on account of its strong refraction of light and oily appearance, is compared by the workmen to "whisky."

The contamination with iron is permanent, and is somewhat stronger than in acid made from the same pyrites in ordinary chambers, precisely because the tower at the same time serves for keeping back the flue-dust. Anyhow this contamination will amount to less than in acid made from pyrites dust in Gerstenhöfer's burner (Bode). According to Hasenclever, his Glover-tower acid contains 0·05 per cent. of iron (*l. c.* p. 506).

If, therefore, acid very free from iron is desired, this can be obtained very easily, in presence of a Glover tower, by taking it direct out of the chambers, for which the tower serves as a dust-retaining apparatus. For most technical purposes the excess of iron found in the Glover-tower acid is altogether unimportant, since anyhow the same material would have furnished an acid containing iron, although a little less of it. Where that excess is of importance, the Glover tower need not be given up; but it must be placed a little further away from the burners, of course with some loss of its concentrating-power.

For concentration in platinum stills up to 170° Tw. the Glover-tower acid has hitherto not been found applicable, hard crusts forming in the platinum dishes. In that case the acid must be brought to 144° Tw. by the waste heat of the platinum stills, as previously.

Under all circumstances, as recognized long since in England, and as proved conclusively from direct numerical results by Bode, the Glover tower remains by far the cheapest apparatus for denitrating and concentrating; it saves all cooling contrivances, and is able to bring the whole of the acid up to 152°, nay, even sometimes up to 160° Tw. That against these advantages there is no set-off of a larger consumption of nitre, has been mentioned previously (p. 423).

An interesting application of the Glover tower is that for utilizing the nitrogen acids remaining in the acid from the manufacture of nitrobenzene; these are used in some works for running down in the Glover tower. Of the utilization of the acid from nitroglycerine mention has been made already (p. 132).

CHAPTER XI.

THEORY OF THE FORMATION OF SULPHURIC ACID IN THE LEAD CHAMBERS.

The behaviour of sulphurous acid towards the various nitrogen compounds in the presence of water, sulphuric acid, &c. having been explained in the previous Chapters, and the so-called chamber-crystals (nitrosulphonic acid or nitrosyl sulphate) especially having been treated of in detail, the exposition of the theories which have been propounded regarding the chamber-process will be a comparatively simple task.

We must from the commencement bear in mind the fact that during the burning of sulphur, whether in the form of brimstone or pyrites, substantially sulphur dioxide (SO_2) alone is formed; the formation of sulphuric anhydride or acid, always occurring at the same time (at least in the case of pyrites), is not taken into account here, being merely a secondary reaction, and not exempting us from the task of explaining the oxidation of the sulphurous acid in the lead chambers. That this does not take place to an appreciable extent by the direct action of the atmospheric oxygen, may at the outset be taken as established. But it is just as certain that the oxygen of the nitre introduced into the process does not suffice to account for it; for the sulphurous acid from 100 parts of sulphur requires another 50 parts of oxygen in order to be oxidized to sulphuric acid, which would correspond to 88·5 parts of nitrate of soda, even if this compound were reduced to nitrogen. But it is well known that, under favourable conditions, only $\frac{1}{30}$ to $\frac{1}{25}$ of the above quantity of nitre is used; and this fact must now be explained.

The first theory on this subject was propounded as early as 1806, by Clément and Désormes ('Annales de Chimie,' lix. p. 329); and it cannot be safely said that, in any essential points, we have at all got beyond the lines they laid down. They had studied the behaviour of sulphurous acid towards a mixture of nitric acid and atmospheric air; and they proved that, even in the crude process then in use (where a mixture of brimstone, saltpetre, and moist clay was heated in a furnace and the gaseous products were conducted into the lead chamber), considerably more oxygen was transferred to the sulphurous acid than the saltpetre contained. They already explained this fact in substantially the same way as it is explained now-a-days, viz. thus:—From the nitre-gas oxidized by atmospheric oxygen, and from the sulphurous acid, sulphuric acid is generated, whilst the nitre-gas is reformed. The nitric acid is only the instrument for the complete oxidation of the sulphur, which in doing its work is not destroyed; for its "basis" the nitre-gas takes up oxygen from the atmospheric air in order to present it to the sulphurous acid in a suitable state; but it remains in its original state at the end of the process of forming the sulphuric acid. The presence of water they explain as necessary, first, for keeping the temperature of the reaction sufficiently low; secondly, for condensing the sulphuric acid as it forms. They also observed in the process the production of white star-shaped crystals, which on contact with water gave out nitre-gas with a strong evolution of heat.

H. Davy showed, in 1812, that the presence of water is absolutely necessary (Berzelius, 'Lehrbuch,' i. p. 471), because in the dry state the gases do not react upon each other; but a small quantity of water added to the mixture of sulphur dioxide and nitrogen trioxide causes the formation of the crystals observed by Clément and Désormes. Davy, therefore, considered that body an intermediate link indispensable for the formation of sulphuric acid; with our present notation we should express his opinion in this way:—

$$\begin{aligned}
&\text{I. } 2\,SO_2 + 3NO_2 + H_2O = 2\,SO_2(OH)(NO_2) + NO;\\
&\text{II.. } 2\,SO_2(OH)(NO_2) + H_2O = 2\,SO_2(OH)_2 + NO_2 + NO;\\
&\text{III. } 2\,NO + 2O = 2\,NO_2.
\end{aligned}$$

Therefore we commence with $3\,NO_2$; and we recover of this $1\,NO_2$ in the equation II., $2\,NO_2$ in the equation III., in order to begin the process over again.

This opinion has been accepted by many other chemists, for instance La Prévostaye (Ann. de Chim. et de Phys. lxxiii. p. 326).

Gmelin also adopts it; he says ('Handbuch,' 5th ed. i. p. 875):—"In all these cases there are mixed in the chamber sulphurous acid gas, vapour of hyponitric acid, arising from the nitric oxide gas and from the oxygen of the air, and aqueous vapour, which is introduced on purpose. There is a crystalline compound of sulphate of nitric oxide with oil of vitriol formed, which sinks down to the bottom of the lead chamber in the shape of a thick white mist and dissolves in the water present there and forms dilute sulphuric acid, nitric-oxide gas being evolved. This nitric oxide gas, with the remaining oxygen of the air, again forms vapour of hyponitric acid, which condenses a fresh quantity of sulphurous acid gas into the crystalline compound, and so forth."

A simpler explanation was given by Berzelius ('Lehrbuch,' i. p. 470). According to him the formation of chamber-crystals is not a necessary intermediate, but only an exceptional case which may happen in some parts of the chamber when steam is wanting; the process, on the contrary, within the chamber consists of the transference of oxygen and water from aqueous nitrous acid (NOOH) to sulphur dioxide, converting it into sulphuric acid, whereby nitric oxide is formed, from which, by means of oxygen and water, nitrous acid is regenerated. Thus:—

$$\text{I. } SO_2+2NO\,.\,OH=SO_2(OH)_2+2NO;$$
$$\text{II. } 2NO+O+H_2O=2NO\,.\,OH.$$

The theory of Berzelius, which is generally accepted, has been completely confirmed by the thorough investigations of Weber. But for some time another theory, that of Peligot, published in 1844 (Annales de Chim. et de Phys. (3) xii. p. 263), contested the palm with it, and was accepted, more especially in France, until very recently; even Kolb ('Études sur la fabrication de l'acide sulfurique,' Lille, 1865, p. 22) adhered to it; and so did Pelouze and Frémy ('Traité de Chimie,' 2nd edition, i. p. 398).

Peligot, like Berzelius, denied that the chamber-crystals had an essential share in the formation of sulphuric acid, or that they appeared at all in the regular process, either in a solid form or in solution. He attributes the oxidation of the sulphurous acid within the lead chamber exclusively to nitric acid, not to the lower oxides of nitrogen. The water is added to decompose the hyponitric acid formed from nitric oxide and atmospheric oxygen, or the nitrous acid formed at the same time, into nitric oxide and [hydrated] nitric acid, and thus to regenerate the only oxidizing agent acting in this process, viz. nitric acid. In watery solution no nitrous acid exists; from a mixture of nitric oxide and atmospheric air not N_2O_3, but only N_2O_4 is formed. These opinions will be made clearer by the following equations (translated into modern symbols):—

$$\begin{aligned} &\text{I. } SO_2+2\,NO_2\,.\,OH &&=SO_2(OH)_2+N_2O_4; \\ &\text{II. } 2\,N_2O_4+H_2O &&=N_2O_3+2\,NO_2\,.\,OH; \\ &\text{III. } 3\,N_2O_3+H_2O &&=4\,NO+2\,NO_2\,.\,OH; \\ &\text{IV. } 2\,NO+2\,O &&=N_2O_4. \end{aligned}$$

The experiments upon which Peligot founded his theory certainly proved that *concentrated* nitric acid oxidizes sulphur dioxide even at the ordinary temperature, hyponitric acid being formed. Sulphur dioxide acts with more difficulty on dilute nitric acid, and only with the aid of heat, nitric oxide being formed. But Weber points out that Peligot's experiments do *not* prove that nitric acid of that degree of dilution which, according to his own theory, must exist in the lead chambers, at the temperature prevailing there, is really decomposed by sulphurous acid. On the contrary, according to Weber's observations, nitric acid of 2 per cent. is not at all changed when cold by sulphur dioxide; there is no appreciable action below 80° C., a temperature which, in normal work, is never approached in the lead chambers.

The classical researches of R. Weber in 1866 and 1867 (Poggendorff's 'Annalen,' cxxvii. p. 543, and cxxx. p. 329) have proved the complete futility, in all points, of Peligot's theory, and have thrown a clear light on the process within the lead chamber. Briefly, he states as follows:—In the chambers, to 100 parts of sulphur, 220 parts of water are used, and from 6 to 8 parts, at most, of nitrate of soda. According to Peligot's equations the liquid at the bottom of the chamber could thus only contain from 2 to 2·3 per cent. of N_2O_5, even without taking into account that, according to him, one third of the nitrogen passes as NO into the atmosphere of the chamber: $3\,N_2O_4=2\,N_2O_5+2\,NO$. [Properly speaking, therefore, only 1·6 to 1·8 per cent. of N_2O_5 could be present in the chamber-acid.] Weber found, by direct experiments, when sulphur dioxide was conducted into nitric acid containing even a higher percentage (viz. 3 per cent.) of N_2O_5, that, at the ordinary temperature, after the lapse of half an hour no sulphuric acid at all had been formed, and extremely little at 40° C (about the temperature of the chambers); whilst in the well-known laboratory experiment in a glass flask, from a mixture of SO_2, NO, atmospheric air, and water there is an easy and instantaneous formation of sulphuric acid; and the lead chambers also produce this acid so quickly that the extremely slow action of nitric acid cannot account for it at all. Furthermore, Weber proved that Peligot was mistaken in supposing that hyponitric acid (N_2O_4) with water merely decomposes to NO and NO_3H, and that N_2O_3 cannot exist in presence of an excess of water; for water which has absorbed vapours of hyponitric acid separates free iodine from a solution of potassium iodide, even when it has been heated to incipient ebullition; it must therefore contain N_2O_3; for neither pure nitric acid nor nitric oxide attacks potassium iodide.

Further, whilst dilute nitric acid has next to no action on sulphur dioxide at the ordinary temperature, there is a strong action between SO_2 and water which has absorbed the vapour of hyponitric acid, or if such water is added to the same dilute nitric acid which at first showed no action, or, more simply, if, instead of pure nitric acid, fuming nitric acid strongly diluted with water be used. *Accordingly, the nitrous acid generated by the contact of hyponitric acid and water oxidizes the sulphurous acid much more readily than nitric acid does; nitrous acid is therefore undoubtedly the primary cause of the reaction for the formation of sulphuric acid when moist air meets sulphurous acid and the vapour of hyponitric acid.* The nitric acid which is formed at the decomposition of N_2O_4 by water remains undecomposed by SO_2 *if much water is present.* Under certain circumstances, however, as will be shown below, the nitric acid is decomposed as well. For the chamber-process the behaviour of N_2O_4 and N_2O_3 towards sulphuric acid of various degrees of dilution with water must also be taken into account, as those gases come into contact with such acids, both in the shape of minute drops suspended in the atmosphere of the chamber and in the shape of the stock collected at the bottom. According to their degree of dilution, the sulphuric acids contain nitrosulphonic acid (chamber-crystals), free N_2O_4, or N_2O_3, as has been explained in detail on p. 370; but all these liquids, when their density is much higher than that of ordinary chamber-acid, are rapidly decomposed by sulphurous acid, sulphuric acid being formed. The decomposition of the absorbed vapours by means of water, for the purpose of forming nitric acid, is therefore quite unnecessary and improbable; but the water must serve for forming the hydrate SO_4H_2, and therefore only in its presence can SO_2 be promptly oxidized by N_2O_3.

It is of importance in practice that the more dilute mixtures containing nitric acid are more easily decomposed by sulphurous acid than concentrated ones. When nitrous acid is dissolved in the pure hydrate SO_4H_2, or even in ordinary vitriol of 170° Tw., the sulphurous acid does not act upon it at all, or at least very incompletely.

When nitric acid is mixed with *dilute* sulphuric acid of varying concentration, it is seen that in a mixture of pure nitric acid of 1·25 spec. gr. with sulphuric acid of 70° Tw. the nitric acid is not decomposed by sulphurous acid in the cold, but quickly on being heated, with evolution of nitric oxide; in the case of stronger acids (from 77° Tw. upwards) the decomposition begins in the cold, and the liquid then contains nitrous acid. Evidently the sulphurous acid first produces nitrous acid in those mixtures, which is proved by their colour and by their action on potassium iodide; and in the *second* stage the nitrous acid yields up oxygen direct to the sulphurous acid, without being compelled, as Peligot assumed, to be redecomposed into nitric acid and nitric oxide—a preposterous assumption. Thus even dilute nitric acid, brought into contact with moderately strong sulphuric acid, may be useful for the chamber-process, as in that case the water is taken away from it, and in the concentrated state it is readily attacked by sulphurous acid; this is just what takes place in the chamber.

Berzelius ('Jahresbericht,' xxv. p. 65) refuted Peligot's opinion that, in the chambers, no nitrous acid is formed from nitric oxide and atmospheric air, but merely hyponitric acid; eudiometric experiments with nitric oxide and oxygen have shown that, according to the excess of one gas or the other, there is more or less condensation, and that in any case there is always a formation of nitrous acid, even with an excess of oxygen.

According to the above argumentation, the water cannot play part which Peligot's theory attributes to it as the essential one, viz. that of decomposing hyponitric and nitrous, and causing the formation of nitric acid. The water no doubt acts essentially by making possible the formation of sulphuric acid proper (SO_4H_2).

With the modern opinions on the essence of acids this is a matter of course; and it is therefore unnecessary to cite the many experiments and arguments adduced by Weber as proof that the water disposes the sulphurous acid to oxidation. It should, however, be added at once that just enough water to form SO_4H_2 is not sufficient, because this strong acid would dissolve the nitrous gas, so as to form nitrosulphonic acid, and would thus withdraw it from the chamber-process; sufficient water must be used to form an acid of no more than 124° or 128° Tw.; then only does the chamber-process go on regularly.

According to Weber's experiments, the following process, therefore, goes on within the chambers. The sulphurous acid is oxidized, mainly by the oxygen of the nitrous acid, which thereby passes into nitric oxide; it does this, however, only when dissolved in water or in dilute sulphuric acid; and such a watery solution is formed either direct from free N_2O_3 or by the decomposition of N_2O_4. In the latter case, at the same time, nitric acid is formed, which can only be decomposed by the mediation of already formed sulphuric acid. The part played by the water has just been explained.

There is an agreement in all essential points, but not in all details, between the opinions of Weber and those published almost contemporaneously by A. Winkler (Untersuchungen &c. p. 20). Winkler also affirms the oxidation of sulphurous acid by nitrous acid; but according to him the part played by hyponitric acid is more essential than that which Weber assigns to it. Winkler believes the latter to be formed principally by the action of air on nitric oxide (contrary to the statements of Berzelius and Weber); it then combines with sulphurous acid and water to form nitrosulphonic acid, which sinks down to the bottom in the shape of the well-known mist, here comes into contact with the dilute hot [?] chamber-acid and dissolves in it, evolving gaseous N_2O_3, which oxidizes a new quantity of sulphurous acid, thereby passing into NO, the latter beginning the process anew. It is clear that this comes to the same thing as the oldest theory of the chamber-process; with Gmelin's explanation especially, quoted above, it agrees almost word for word.

From Weber's opinions the following formulæ can be derived:—

I. $SO_2+N_2O_3+H_2O \quad = SO_2(OH)_2+2\,NO$;
II. $2\,NO+O \quad = N_2O_3$;

and as secondary reactions :—

III. $2\,NO+2\,O \quad = N_2O_4$;
IV. $N_2O_4+H_2O \quad = NO\,.\,OH + NO_2\,.\,OH$;
V. $4\,NO_3H+5\,SO_2+3\,H_2O = 5\,SO_2(OH)_2+2\,NO+N_2O_3$;

Winkler's opinions can be represented thus :—

I. $N_2O_3+SO_2+H_2O \quad = SO_2(OH)_2+2\,NO$;
II. $2\,NO+2\,O \quad = N_2O_4$;
III. $2\,N_2O_4+2\,SO_2+H_2O \quad = 2\,SO_2(OH)(NO_2)+N_2O_3$;
IV. $2\,SO_2(OH)(NO_2)+H_2O = 2\,SO_2(OH)_2+N_2O_3$.

The secondary reactions III. to V. of Weber's theory at all events take place here as well.

Winkler's theory is rather more complicated than that of Berzelius and Weber; moreover it only reckons with the reaction $2\,NO+2\,O=N_2O_4$, and leaves out of sight the other, certainly existing, reaction, $2\,NO+O=N_2O_3$. Winkler himself only regards it as *probable,* without giving any proof of it, and no doubt does not accentuate the deviation of his opinions from those of Berzelius and Weber.

Whichever formulæ may be chosen for explaining the chamber-process, a certain difficulty will always remain in the assumption of a simultaneous oxidation of nitric oxide and reduction of higher oxides to nitric oxide. But although both processes undoubtedly take place at the same time, this may happen in the same chamber under different conditions: when in a certain part nitrous gas is reduced to nitric oxide, sulphurous acid vanishes at that part, and the excess of oxygen present everywhere can now oxidize the nitric oxide again; by currents, diffusion, &c. fresh sulphurous acid is brought in, and the process commences again. Besides, in any case the law of the action of masses comes into play, which may even cause qualitatively inverse reactions between the same substances, when their relative *quantities* are changed—for instance, the reduction of ferric oxide and formation of water in an atmosphere of hydrogen, and the oxidation of iron in an atmosphere of aqueous vapour. In a similar way the conditions in different parts of the chamber may differ so that both reactions take place, the oxidation as well as the reduction of the nitrogen compounds.

The question may now be raised, *Which of the oxides of nitrogen* is principally present in the atmosphere of the chamber? or are they there in a state of equilibrium? It is probable that in the atmosphere of the chamber the highest and the lowest oxide in question here exist only momentarily and in certain places. This holds good of the nitric acid, because it is reduced immediately on entering the chamber by the sulphurous acid with the assistance of the aqueous vapour and of sulphuric acid, and because, on the other hand, the lower oxides of nitrogen cannot unite with oxygen to reform nitric acid, but, at the most, only hyponitric acid. On the other hand, the nitric oxide, NO, can only exist momentarily, although we consider it as continuously coming into existence, because there is oxygen present all over the chamber, which immediately oxidizes it again. But as far as nitrous and hyponitric acid (nitrogen trioxide and tetroxide) are concerned, it is quite possible that in many places they are in excess; and since there is always an excess of oxygen present as well, the gas, when in equilibrium, will contain those two nitrogen oxides. If the composition of the gas could be fixed at any given moment, in a normally working chamber, the molecules just then present of N_2O_3 and N_2O_4 would greatly exceed in number those of NO. This is also proved by the yellow, or even dark red, colour of the gas as seen through the windows of the lead chambers. Only in "pale" chambers will nitric oxide (NO) predominate. Which of the two oxides, N_2O_3 or N_2O_4, is in greatest quantity in a normal chamber is a different question. Most probably both of them are always present; but according to Weber the amount of N_2O_3, according to Winkler that of N_2O_4 would be the greater. The author believes he has good reason for assuming that in a *normally* working chamber, where there is neither too much nor too little oxygen, the nitrous acid greatly predominates over the hyponitric acid. This can be inferred, 1st, because according to Winkler's and the author's own experiments nitric oxide in the presence of sulphuric acid of moderate strength, which is everywhere present in the chamber in the shape of a mist, is not oxidized beyond N_2O_3 even by an excess of oxygen; 2nd, because the nitrous vitriols analyzed by the author never showed more than traces of higher oxides than N_2O_3 (that is, nitrosulphonic acid proper), whilst, for instance, when the pure hyponitric acid given off by heating lead nitrate was absorbed by sulphuric acid, quite normally a mixture of equal parts of N_2O_3 and N_2O_5 was found. The different results found by several chemists (Kolb, Winkler, Hurter) with respect to their nitrous vitriols can be referred to faulty analytical methods—with certainty in some cases; and in others the matter at least demands reinvestigation now that the analytical methods have been so much improved. It may also have been the consequence of irregular work. Where the formation of sulphuric acid ceases almost entirely in the last chamber, the condition for forming nothing but N_2O_3 is absent; and in that case first N_2O_4, and then, by its contact with water, also N_2O_5 will be formed.

To be sure, if the free oxygen should be used up, the sulphurous acid, then in excess, will at once reduce N_2O_3 and N_2O_4 to NO, and the chamber will turn pale. The same will happen when too much air enters, because then the gas gets too much diluted. When there is a deficiency of sulphurous acid (which in normal work ought not to happen), much of the nitrogen will be converted by the oxygen in excess to N_2O_4, which will be split up with the water into $N_2O_3 + NO_2 . OH$. This, however, can only happen when the chamber-acid is very dilute; otherwise from the first only N_2O_3 is formed (see above), and therefore no $NO_2 . OH$ will appear.

There still remains for consideration another very important matter, which has found no expression in any of the above formulæ and statements. According to all the equations given above, the oxidation of sulphurous acid by the nitrogen acids is effected in this way:—They are not reduced beyond the stage of nitric oxide; and since nitric oxide, so long as it meets with air in excess, at once passes again into N_2O_3 and N_2O_4, there ought to be, if the chamber is in proper working order and with the proper excess of oxygen, no loss of nitrogen oxides whatever, and the stock once introduced into the chambers ought to last for ever. This is well known not to be the case; even at those works where the best Gay-Lussac towers are employed, and at the same time the proper composition of the kiln-gas is maintained, at which, therefore, all the nitrogen compounds in the Gay-Lussac tower ought to be recovered and restored to the chambers—even there, when the working progresses favourably, nearly 3 parts (mostly nearer 4 parts) of nitrate of soda must be introduced for every 100 parts of sulphur burnt.

The sources of this *loss of nitre* may certainly be of various kinds. In the first place, the absorption of the nitrogen oxides in the Gay-Lussac tower may not be quite perfect. This cannot amount to a great deal, if the tower is sufficiently large and is sufficiently fed with strong and well-cooled acid; but when only one of these conditions is neglected, there will be at once a considerable loss of nitrogen acids, and consequently more waste of nitrate of soda. If arsenious acid occurs in considerable quantity in the sulphuric acid used for the Gay-Lussac tower, some nitric oxide will be lost, because the arsenious acid will at least partly be oxidized to arsenic acid at the expense of the nitrous acid. With an excess of oxygen, such as is or should be always present, the nitric oxide certainly ought to be reoxidized at once to N_2O_3 and to be dissolved in the tower-acid; but, owing to insufficient contact and time, this reaction will probably never be complete. Much greater losses, through the formation of nitric oxide, will be caused by any sulphurous acid getting into the Gay-Lussac tower; but this, in normal working, is not likely to occur to an appreciable extent. At any rate it seems to be established that even with a large excess of oxygen there is still some nitric oxide left, although in very small quantity; this is to be attributed either to imperfect mixture of the gases or to a phenomenon of dissociation. It need hardly be mentioned that, owing to the almost perfect insolubility of nitric oxide in sulphuric acid (p. 365), all that in this state gets as far as the Gay-Lussac tower escapes recovery.

Secondly, nitrogen oxides may go along with the finished sulphuric acid taken away from the chambers. This source of loss exists only to an extremely small extent for manufacturers working with the Glover tower, who pass all their chamber-acid through the tower, and also for all others in a totally insufficient degree to explain the actual loss of nitre. There must therefore be another source of the latter; and this seems to point to the fact that under certain conditions the nitrogen compounds are reduced to N_2O or even to N, in which state they cannot be reoxidized by the atmospheric oxygen, but must escape along with the other inert gases of the chambers. Pelouze already (Annales de Chim. et de Phys. lx. p. 162) pronounced the opinion that, in case of a want of oxygen in the atmosphere of the chamber, moist sulphurous acid may cause a reduction of the nitric oxide to nitrous oxide, since, according to him, a gaseous mixture of 2 vols. NO and 1 vol. SO_2 in the presence of water is condensed to 1 vol. N_2O within a few hours. Weber (Poggend. Ann. cxxx. p. 329) could not entirely confirm this; he found the formation of nitrous oxide by the mutual reaction of the above two gases to be far too slow to account for the loss in the chambers, and still less as the conditions there are different from those of Pelouze's experiments, viz. as the oxygen of the chamber-acid is never completely used up. According to Kuhlmann (p. 422) the reduction of nitric oxide goes even as far as nitrogen; but he worked under conditions never occurring here, viz. in the presence of spongy platinum; and therefore we need not, in this connexion, pay any attention to his results. Pelouze's explanation of the loss of nitre is certainly not valid for a normally working chamber; so that another explanation must be sought for.

Now, according to Weber, certainly even nitrous acid is easily reduced to nitrous oxide, but only *in presence of an excess of water*. This is proved by the fact that a *dilute* solution of pure nitrous acid with a watery solution of sulphurous acid produces almost twice the quantity of sulphuric acid that corresponds to the equation

$$N_2O_3 + SO_2 + H_2O = 2NO + SO_2(OH)_2.$$

The following process must have occurred:—

$$N_2O_3 + 2SO_2 + 2H_2O = N_2O + 2SO_2(OH)_2;$$

and, by collecting the evolved gas, Weber in fact convinced himself that it was not nitric oxide, but nitrous oxide.

It must, however, be distinctly pointed out that this reaction only happens if *very much water* is present. Even if, instead of water, dilute sulphuric acid meets sulphurous acid and nitrous vapours, what is formed is almost entirely nitric oxide. The latter is also generated, apart from the sulphuric acid, when sulphur dioxide, nitrogen trioxide, and *only as much water as is present in the chamber under normal circumstances* meet together. On the other hand, under the same circumstances as nitrous acid, even nitric acid can be reduced to nitrous oxide by sulphurous acid, but with more difficulty.

This behaviour of the nitrogen acids explains why during disturbances of the work, when the quantity of sulphuric acid falls and that of water in the chamber-air is thereby relatively increased, the chambers become pale and large losses of nitre occur. This further explains the fact that a new chamber is more easily got into working order when started with dilute sulphuric acid than when started with water; in the latter case a large quantity of the nitre-gas will be reduced to nitrous oxide by contact with the water and will be lost, until at length a sufficiently strong sulphuric acid has collected at the bottom of the chamber to obviate this. But even in normal working the conditions for the formation of nitrous oxide cannot be entirely excluded. Especially near the inlets for the steam (that is, in the very moist parts of the chamber-space) there is probably a formation of N_2O by the reaction of SO_2 on N_2O_3 in presence of an excess of water.

From all those sources taken together, and considering that an absolutely normal working of the process cannot be attained even with the greatest care, is to be explained why a certain loss of nitre in manufacturing sulphuric acid is unavoidable, as well as the fact that since the introduction of a more rational style of working that loss has become much smaller. The absorption of nitre-gas by strong sulphuric acid, the possibility afforded by this of allowing the former to predominate in the last chamber, and the control of the kiln-gas by analysis are the principal items of progress in this respect.

The following concluding observations on the theory of the chamber-process seem to present some interest. It is a matter of experience that the reactions above explained, consisting in reductions and oxidations, do not take place instantaneously, but require a certain *time*, in order to produce a maximum of sulphuric acid with a minimum of nitrogen oxides. This is demonstrated by the fact that for a certain quantity of sulphur burnt there must be a minimum of *chamber-space*, in order to obtain the best possible yield of sulphuric acid. This question has been spoken of on page 294. That is to say, in order that a certain number of molecules of sulphurous acid may be oxidized to sulphuric acid by means of the stock of nitrous acid present by a succession of reductions and oxidations, but not by reduction below nitric oxide, there must be a sufficient time afforded for the necessary inversions of the reaction to take place. What this time amounts to, can be calculated from the chamber-space; but the uncertainty of the amount of the chamber-space, which can only be settled empirically, must make the time result uncertain as well. Such calculations have been made by Schwarzenberg (p. 398) and Bode (note to his translation of H. A. Smith's pamphlet, p. 108). The first arrives at the conclusion that a volume of gas equal to the total chamber-space is introduced and used up once every 5¾ hours, that therefore, under the conditions considered by him normal, the formation of sulphuric acid is completed in 5¾ hours, and that the nitrous acid is the intermediate agent for the combination of sulphurous acid with a quantity of oxygen exceeding its own oxygen 28·8 times; when hyponitric acid is assumed to be the agent in question, the quantity of oxygen used up amounts to 21·9 times that of the hyponitric acid. But as in the normal chamber-process those acids do not give up the whole of their oxygen, but the nitrous acid only one third, the hyponitric acid one half of it, the number of the alternate reductions and oxidations in the case of nitrous acid will mount up to $28{\cdot}8 \times 3 = 86{\cdot}4$, and in the case of hyponitric acid to $21{\cdot}9 \times 2 = 43{\cdot}8$. Bode, starting from different premises, arrives, for a normal process, at 3·43 hours' time, and, assuming N_2O_4 as the agent, at 22·8 alternate reductions and regenerations of the same.

We shall now carry out the calculation on the basis of the fact mentioned on p. 295, and established by manifold experience of the largest acid-makers, viz. that a chamber-space of 1·2 cubic metre per kilogram (equal to 19·2 cubic feet per lb.) of the sulphur contained in the pyrites, charged every 24 hours, is quite sufficient for a maximum yield of acid and a minimum consumption of nitre, presupposing the existence of a Gay-Lussac and a Glover tower and the employment of rich ores (say, with 8 per cent. by volume of sulphur dioxide in the kiln-gas). If the ore contains 48 per cent. of sulphur, of which 4 per cent. remains in the cinders, and 44 per cent. is really given off as gas, of each 1000 grams. of sulphur only $\frac{44}{48} = 917$ grams will really arrive in the chambers in the shape of sulphurous acid. (The small quantity of SO_3 formed directly, comp. p. 242, can be neglected in this calculation.) This quantity corresponds to $\frac{917 \times 64}{32}$ sulphur dioxide = 1834 grams. Now 1 gram SO_2, at 0° C. and 760 millims. barometric pressure, fills the space of 0·348 litre; 1834 grams, therefore, 638·2 litres. If 8 per cent. by volume of this gas is contained in the burner-gas, the total volume of the latter for 1834 grams SO_2 will thus be

7977·5 l. at 0° and 760 millims.,

or, at the chamber-temperature of 50° C.,

$$\frac{(273+50)7977{\cdot}5}{273} = 9438{\cdot}5 \text{ litres.}$$

To this must be added the increase of volume caused by saturation with aqueous vapour, by which the volume becomes

$$V_1 = \frac{V \times 760}{760 - e},$$

where V is the volume, at the temperature of the experiment, just found, and e the tension of the aqueous vapour for the same temperature; in this case, for 50° C., e is $=92$ millims.; the equation thus becomes

$$V_1 = \frac{9438{\cdot}5 \times 760}{760 - 92} = 10738{\cdot}4 \text{ litres.}$$

Now we have assumed that for this volume of gas there is a chamber-space of 1·2 cubic metre=1200 litres; within 24 hours, therefore, the chamber must be filled $\frac{10738{\cdot}4}{1200} = 8{\cdot}949$ times; or, in other words, the gas will take $\frac{24}{8{\cdot}949} = 2{\cdot}682$ hours in order to travel from the entrance of the chambers to their outlet; and it must, therefore, during this time give up all its sulphurous acid condensed to sulphuric acid. If we would make the calculation more exact, we should have to take the volume of nitrogen into account; but, in the first place, this volume is proportionally so small that the results would not be materially changed; and, secondly, we do not know in which shape (as N_2O_3, N_2O_4, $SO_2(NO_2)(OH)$, &c.) the nitre-gas is present in the chamber-atmosphere, and therefore we cannot calculate its volume. Further, for a precise calculation, we ought to take into account the deviation of the outer atmospheric pressure from 760 millims. For obvious reasons, however, we abstain from doing that in this instance. Nor must it be forgotten that by far the greater portion of the sulphuric acid is formed in the first half of the chamber-space, and therefore the action is very unequally distributed.

The quantitative amount of action which the nitre-gas exerts in the chamber, or the number of reductions and oxidations undergone by the same, will be found by the following calculation (in which we assume a consumption of 4 parts of pure sodium nitrate to 100 parts of sulphur burnt, which figure in well-managed works is not even reached) :—The 100 sulphur yield 200 parts of SO_2, and require another 50 oxygen, in order to form sulphuric acid, along with the necessary water, about which we need not trouble here. The 4 parts of nitrate for this object give up, in the first instance, that part of their oxygen which nitric acid loses when passing into hyponitric acid—that is,

$$\frac{4\times 16}{2\times 85}=0{\cdot}377 \text{ oxygen,}$$

which must be deducted from the above-mentioned 50 parts to begin with, and brings it down to 49·623 parts, which have to be supplied by reduction and regeneration of the hyponitric acid formed. Now hyponitric acid from 4 parts of sodium nitrate can yield up $\frac{4\times 16}{85}=0{\cdot}753$ part of oxygen in order to be reduced to nitric oxide (NO); and it will therefore have to be regenerated $\frac{49{\cdot}623}{0{\cdot}753}=65{\cdot}9$ times in order to accomplish its purpose.

This calculation has been made on the assumption that in the lead chamber hyponitric acid is the essential active principle. But if (in accordance with the opinion of Berzelius, Weber, and the author himself) nitrous acid be assumed as such, by reduction of nitric acid to nitrous acid there is obtained, from 4 parts of sodium nitrate,

$$\frac{4\times 16}{85}=0{\cdot}753,$$

which, deducted from 50 parts, leaves 49·247 parts of oxygen to be supplied by the further action of nitrous acid. The nitrous acid from 4 parts of sodium nitrate, when reduced to nitric oxide, yields $\frac{4\times 16}{2\times 85}=0{\cdot}377$ oxygen, and is therefore reduced and regenerated

$$\frac{49{\cdot}247}{0{\cdot}377}=130{\cdot}6 \text{ times}$$

in order to carry out the work in the chambers.

This can also be expressed as follows:—The gas evolved out of the nitre, under the above conditions (now attained as a *minimum* in all well-managed works), is, assuming the truth of the hyponitric-acid theory, utilized 65·9 times—assuming that of the nitrous-acid theory, even 130·6 times, before it is lost in the shape of nitrous oxide, possibly as nitrogen, or by the escape of higher oxides or nitrogen in spite of the Gay-Lussac tower, or by being carried away in the chamber-acid &c. That this result is much more favourable than those of Schwarzenberg and Bode (quoted above) is caused by the former assuming a consumption of 6 parts nitre to 100 parts of sulphur, the latter of 4 parts of nitre to 100 parts of strong vitriol, or 12 parts to 100 parts of sulphur—figures which afford a telling proof of the great progress made in the meantime in the manufacture of sulphuric acid.

In the modern manufacture of sulphuric acid there is always to be taken into account the recovery of a large portion of the oxides of nitrogen, by which these are compelled to make their way through the chambers more than once. The absolute quantity of the oxides of nitrogen present at any given time in the chambers is in this case even larger than with the former process without recovery of nitrogen, since in the new process the last chamber can and must be kept much richer in nitre-gas than in the old process. Evidently, to the newly introduced quantity of nitre that quantity must be added which is re-introduced into the process by the Gay-Lussac-tower acid (the nitrous vitriol), and, in the case of a Glover tower, also that which is obtained by complete denitration of the chamber-acid. It is impossible to make a general statement on the quantities of nitre proceeding from these sources, since they differ in each individual set of chambers, and even in the same set at different points; but it may be safely assumed that the quantity of nitre circulating in a set of chambers is *at least* twice the quantity freshly introduced. For a special case (which, to be sure, only holds good locally) Hurter (Dingler's Journal, ccxxvii. p. 565) calculates the quantity of nitre in circulation at fourfold the quantity newly added—viz. at 19·61 parts to 100 parts of sulphur burnt, as against 5·04 parts freshly added.

CHAPTER XII.

THE PURIFICATION OF SULPHURIC ACID.

THE vitriol of trade, as it is produced in the chambers, always contains a number of impurities, partly owing to the raw material, especially the pyrites, employed, partly from the nitre, the water, the lead of the chambers, &c., not to speak of intentional adulterations. Since this acid, if at all, has to be purified at the stage at which we have now arrived, viz. as chamber-acid, before being concentrated, we shall now treat of this matter, although, in the great majority of works, the chamber-acid is never purified, nor is there any occasion for it. For the sake of completeness, we shall here describe also the manufacture of pure distilled oil of vitriol, although this already presupposes the concentration of acid on a large scale, to be described hereafter.

The essential impurities of chamber-acid may consist of:—arsenic acid, arsenious acid, antimonic oxide, selenium, thallium, lead, iron, copper, lime, aluminium, alkalies; further, sulphurous acid, nitric acid, nitrous acid, organic substances. According to Kuhlemann, for instance (Wagner's Jahresb. 1872, p. 253), the acid of two Harz works contained to each 100 grams SO_3:—

	a.	*b.*
Arsenic.........	0·0088 grm.	0·0174 grm.
Antimony......	0·0394 „	trace.
Copper	0·0013 „	„
Iron	0·0081 „	not estimated.
Zinc	0·0087 „	„
Lead...........	trace	0·0231 grm.

According to Bräuning (Preuss. Zeitschr. für Berg.- &c. Wesen, 1877, p. 142) the chamber-acid at Oker in the Harz contains on the average 0·05 per cent. of arsenic and 0·008 per cent. of antimony. *Selenium* has been found in sulphuric acid by Kuhlmann, Scheurer-Kestner, Lamy, and others (Wagner, ib. p. 246); its occurrence in the flue-dust and the chamber-deposit are well known.

Most of these substances occur partly in too small a quantity in the vitriol to be injurious, partly they are without any influence for most uses of the sulphuric acid; the lead, for instance, is almost entirely precipitated on diluting the acid,—the iron during its concentration in the platinum still, in the shape of pink crystals of anhydrous ferric sulphate. Special importance attaches, at least in some cases, to the removal of arsenic, especially when the pyrites contains very much of it, and to that of the nitrogen compounds—the latter when the acid has to be concentrated in platinum vessels.

The purification of Sulphuric Acid from Arsenic.

Arsenic is found rarely, and never in more than traces, in acid which has been made from brimstone; most of the latter material, by far, is used where acid free from arsenic is wanted. On the other hand nearly all kinds of pyrites contain arsenic; and the acid obtained from them is therefore always arsenical—but in very different degrees, according to the percentage of arsenic in the pyrites and to the mode of manufacture.

The percentage of arsenic in pyrites is stated very differently: whilst most analyses of the ordinary ores only show "traces" up to fractions of 1 per cent., H. A. Smith asserts that he has found much larger quantities in the ores most commonly employed, viz. in Westphalian pyrites 1·878, in Belgian pyrites 0·943, in Spanish 1·651, in Portuguese 1·745, in Norwegian 1·649–1·708 per cent. of arsenious acid. These analyses are not quite to be relied upon, since their results differ so much from all others. Nor must it be left out of sight that Smith, whenever he speaks of "arsenic," does not mean metallic arsenic, but arsenious acid, As_2O_3. This has been overlooked by some who have used his pamphlet; and he has himself confounded the two things by taking the figures from Richardson and Watts's 'Chemical Technology' which refer to As, as As_2O_3. [Some time after the above had been written, Hjelt's paper appeared in Dingler's 'Journal,' ccxxvi. p. 174. Hjelt has likewise noticed the confusion of Smith's "arsenic" (by which he means arsenious acid) with metallic arsenic. He himself finds in

Westphalian pyrites no more than 0·30, in Norwegian only traces, in Spanish pyrites on an average 0·91 per cent. of As.]

Smith further undertook the task of following up the arsenic through the whole course of manufacture; and he obtained the following results. A portion of the arsenic remains in the cinders; a much more considerable portion is met with in the deposit found in the gas-pipes leading from the pyrites-burners to the chambers, along with sublimed sulphur; a good deal of arsenic is found in the sulphuric acid itself and in the chamber-mud. This is further evidenced by a considerable percentage of arsenic in the muriatic acid; a little arsenic is also found in the sulphate of soda, a good deal as a deposit in the pipes conveying the muriatic gas to the condensers—also in the coke packing of the latter, and even in the gas escaping behind the condensers—also, lastly, in the sulphur regenerated from the soda-waste by Mond's process, but not after the sulphur has been refined; nor was there found any arsenic in the soda-ash itself. Smith's average results were the following:—

	Per cent. of As_2O_3.
1. Pyrites (hard Norwegian)...........	1·649
2. Cinders of the same	0·465
3. Sulphuric acid	1·051
4. Deposit in the gas-pipe..............	46·360
5. Deposit in the chamber..............	1·857
6. Hydrochloric acid	0·691
7. Coke packing of the condensers ...	2·886
8. Sulphate of soda	0·029
9. Soda-waste............................	0·442
10. Soda-ash..............................	none
11. Recovered sulphur....................	0·700
12. Recovered sulphur purified	none

Even the gas escaping from the condensers into the chimney contained in 100 cubic metres 0·036 grm., per hour 0·325, daily 7·794 grms.; and the air of the chimney contained 0·0197 grm. per 100 metres—a quantity not to be neglected [if Smith's analyses could be relied on!].

Hjelt (*l. c.*) found, when employing Spanish pyrites with 0·91 per cent. of arsenic (As), in the cinders 0·19 per cent., in the sulphate none, in the hydrochloric acid:—(*a*) pan-acid of 38° Tw., 0·066 per cent.; (*b*) drier acid of 32° Tw., 0·014 per cent. As. The latter contains less, because the arsenical chloride mostly volatilized in the pan.

Smith makes a calculation which (though he and those employing his numbers have failed to notice it) clearly demonstrates the incorrectness of his analyses.

There are said to have been contained in 100 parts of pyrites	1·649	As_2O_3.
These produced 140·875 parts of sulphuric acid, at 1·051 per cent.	1·481	„
Now the cinders are said to have contained 0·465 part of As_2O_3; and taking them at 75 per cent. of the weight of the pyrites, say	0·349	„
We obtain altogether	1·830	„

Against 1·649 part said to be contained in the original pyrites; but then no account is taken here of the fact that a very large portion of the arsenic is found in the flue-dust, which, according to Smith himself, contains upwards of 46 per cent. of As_2O_3. His analyses, therefore, are not trustworthy.

Of course, even with the same raw material, the arsenic in the sulphuric acid will vary, according to whether the gas-pipe leading from the burners to the chambers offers more or less opportunity for depositing arsenical flue-dust. When employing a Glover tower the acid contains rather less arsenic, because a large portion of it is deposited at the bottom of the tower in the shape of mud.

Filhol and Lacassin found in three samples of "pure" commercial sulphuric acid, per kilog.:—1·2870 grm.; 0·5691 grm.; traces of As_2O_3 (Wagner's Jahresb. 1862, p. 212). Further estimations of arsenic in commercial sulphuric acid, according to Schnedermann, Kerl, Filhol, &c., will be mentioned below; those of Kuhlemann and Bräuning have already been given. In the most recent paper on this subject, that of Hjelt, are the following statements:—When Spanish pyrites with 0·91 per cent. of As was used, there was contained, for each 100 parts of SO_4H_2, in the

Chamber-acid	0·202 As,	of which		0·040	as As_2O_5.
Glover-tower acid	0·331	„	„	0·041	„
Gay-Lussac-tower acid ...	0·341	„	„	0·132	„
Acid of the last chamber .	0·019				

The higher proportion of the Glover-tower acid comes from the arsenic contained in the gas; the accession of arsenic in the Gay-Lussac tower is, of course, caused by the oxidizing action of the nitrous vitriol.

According to Davis (Chem. News, xxxvii. p. 155), in the Glover tower all arsenic acid is reduced to arsenious acid by the burner-gas, and in the Gay-Lussac tower all is again converted into arsenic acid. This assertion is not merely refuted by the analyses of Hjelt just quoted, but also by many analyses of the author's, in which he always found both degrees of oxidation of arsenic at the same time.

In most cases of the employment of sulphuric acid a small percentage of arsenic is of no consequence—for instance, in superphosphate, or in sulphate of soda to be used for alkali- or glass-making. In the latter case certainly most of the arsenic passes over into the muriatic acid and can be traced there. When the muriatic acid is used for generating chlorine, the arsenic does no harm; for although it probably passes over, at any rate partly, into the chloride of lime, it will only occur in this as the insoluble and innocuous calcium arseniate. Much more harm does arsenic in the sulphuric or muriatic acid which is employed in any way in the food industries, for instance in the manufacture of starch-sugar, in the formation of molasses, for pressed yeast, for washing the regenerated char of sugar-works, &c. A. W. Hofmann has reported a poisoning-case in which bread was contaminated with arsenic by the use of arsenical muriatic acid along with soda to make the dough rise. It is unnecessary to speak of medicinal uses, since for them crude sulphuric or muriatic acid is never supposed to be employed.

But even for some purely technical uses arsenic in sulphuric (or muriatic) acid is not allowable:—on the one hand, for the preparation of certain colours, for tinning iron (sheet iron cleaned with arsenical sulphuric acid is here and there covered with spots of reduced arsenic, which will not take the tin coating,—see Gossage in Hofmann's Report by the Juries, 1862, p. 12); on the other hand, for the manufacture of preparations which serve for food or medicine, and into which a portion of the arsenic might pass over. To these belong tartaric, citric, phosphoric acids, milk of sulphur, sulphide of antimony, &c. Even in Doebereiner's lighting-machines arsenical acid must be avoided, since the arseniuretted hydrogen evolved in them would soon spoil the platinum sponge. It has also been observed that ammonium sulphate made from ammoniacal gas-liquor by means of strongly arsenical sulphuric acid turns yellow, no doubt in consequence of the formation of sulphide of arsenic. It will be shown later on, in describing Deacon's chlorine process, that arsenical sulphuric acid seems to do great harm in it also.

Probably sulphuric acid intended for alkali or manure works is never submitted to any purification at all; and for most purposes where the acid ought to be free from arsenic, consumers employ the acid made from brimstone. Also in making acid from pyrites a large portion of the arsenic is deposited in the connecting-pipes between the pyrites-burners and the chambers, more especially when long cooling-flues or chambers are used, as is at any rate the case in the absence of a Glover tower. Sometimes for this special purpose a small antechamber is provided, whose acid, of course, must not be run into the main chamber. Along with arsenic in all these apparatus selenium and thallium are found, if such are contained in the pyrites; and it is in this way only that they are obtained. At most factories there is only this superficial purification of the vitriol from arsenic. At Freiberg, according to Bode (Dingler's Journal, ccxiii. p. 26), by the enlargement of the flue-dust-chambers, the percentage of arsenious acid in the chamber-acid, previously amounting to $\frac{1}{4}$ to $\frac{1}{2}$ per cent., has been lowered to 0·05 per cent.; the remainder of the arsenic is recovered from the collecting-places and sold as such.

In some cases, however, it is of importance for the producers of strongly arsenical vitriol to make it more salable; and a number of methods of purification have been proposed with this object. None of them seems to produce an acid absolutely free from arsenic, but sufficiently so for all practical purposes. Bloxam (Pharm. Journal, [2], iii. p. 606), by employing his electrolytical method for the discovery of arsenic, found that all samples sold as "chemically pure" contained traces of it, and that acid absolutely free from arsenic cannot be obtained in any other way than from pure sulphur dioxide and nitric oxide in glass apparatus at a low temperature, avoiding all cork or india-rubber; the gases themselves must be evolved cold or at a very moderate heat.

The following methods have been employed for the separation of arsenic from sulphuric acid.

(1) *Distillation* of the vitriol (Bussy and Buignet, Dingl. Journ. clxii. p. 454) is said to effect this purpose, even more completely than precipitation by sulphuretted hydrogen, provided that the arsenic is all present as arsenic acid, which remains entirely behind in the residue; if, however, arsenious acid be present, it is carried over with the vitriol. Since the sulphuric acid of commerce mostly contains arsenious acid, it is to be treated with nitric acid, in order to convert all the arsenic into arsenic acid; then the acid is to be mixed with a little ammonium sulphate (in order to destroy the nitrous acid), and distilled. In this case the arsenic is said to be removed more completely than by sulphuretted hydrogen or barium sulphide; at the same time the dilution of the acid, necessary in the latter case, is avoided. But the distillation of sulphuric acid is an operation not yet introduced at all on the large scale, and is not applicable for the purification of chamber-acid.

According to Blondlot (Compt. Rend. lviii. p. 76), the employment of ammonium sulphate is objectionable, because by an excess of it arsenic acid is reduced again. He therefore recommends heating the acid with peroxide of manganese or potassium permanganate. Bussy and Buignet deny that an excess of ammonium sulphate reduces arsenic acid (Compt. Rend. lviii. p. 981). Maxwell Lyte (Chem. News, ix. p. 172) says the statement of Bussy and Buignet, that arsenic does not distil over unless present as arsenious acid, is correct; but in order to obtain from the first a product completely free from nitrogen compounds, he destroys the latter by adding to the sulphuric acid ¼ to ½ per cent. of oxalic acid, heating in a porcelain dish to 110° C. with continuous stirring, cooling down to 100° C., and adding potassium bichromate in the state of powder or as a solution in sulphuric acid, till the green colour has been changed to greenish yellow and the presence of free chromic acid is thus indicated. All the arsenic is now converted into arsenic acid; and on distillation a perfectly pure acid is at once obtained. Permanganate of potash performs the same service, but is more expensive.

(2) *Removal of the arsenic as trichloride.*—This boils at 125° C.; it is therefore completely volatilized on heating, long before the sulphuric acid has begun to boil: this process can be used without diluting the latter. With this object Otto and Löwe proposed heating the acid with common salt (Dingler's Journal, cxxxii. p. 205)—Graeger, heating with barium chloride, because the action in this case is not so rapid (ib. clv. p. 236); Buchner (in 1845) recommended conducting a current of hydrochloric acid gas into boiling sulphuric acid and expelling the hydrochloric acid by heating in the open air. Bussy and Buignet have certainly proved that in this way acid free from arsenic cannot be obtained; but Buchner (Chem. Centralbl. 1864, p. 600) asserts that this comes from the presence of arsenic acid, and that an acid entirely free from arsenic is obtained by first reducing the arsenic acid contained in the vitriol by heating it with charcoal, when the sulphur dioxide evolved causes the reduction; this can be done at the same time with introducing the current of hydrochloric acid gas. If Buchner's statement is correct, the troublesome operation of distilling the vitriol is unnecessary. Schwarz (Wagner's Jahresb. 1865, p. 232) heats the acid for some time with 1 per cent. of common salt and $\frac{1}{4}$ per cent. of charcoal dust under a chimney with a good draught—which comes to the same thing, and appears to be more convenient; but on carrying it out on the large scale, great difficulties arise from the fact that the process does not work with dilute acid, and that with the introduction of common salt into concentrated acid the glass retorts often crack. (See H. A. Smith's pamphlet; he is unacquainted with the addition of charcoal recommended ten years previously, and therefore, of course, finds arsenic left in the sulphuric acid at the end of the operation.) According to Tod (Liebig's Jahresb. 1856, p. 292), if a current of HCl is introduced, heating to 130°–140° is sufficient, while if common salt be employed the acid must be heated to 180°–190° C., in order to expel the arsenic trichloride.

(3) *Precipitation of the arsenic as sulphide.*—This is the only operation carried out on a manufacturing scale which offers the additional advantage that, apart from the arsenic, several other impurities are precipitated (such as lead, antimony, selenium) and others are destroyed (such as sulphurous, nitrous, and nitric acids).

Under all circumstances the precipitation must take place at a moderate concentration of the acid; too highly concentrated sulphuric acid is decomposed by sulphuretted hydrogen with separation of sulphur, according to the equation

$$3H_2S + SO_4H_2 = 4H_2O + 4S;$$

the acid must therefore be in the state of chamber-acid, or, better, not above 106° Tw. When the arsenic is present as arsenic acid, it is much more slowly precipitated than when present as arsenious acid.

The simplest way for practice on the large scale appears to be, to generate the sulphuretted hydrogen within the liquid itself; and we shall first consider the methods and proposals made for this purpose.

(*a*) *Precipitation by barium sulphide.*—Proposed by Dupasquier in 1845, this process is said to be carried out practically at Chessy (Hofmann's Report by the Juries, 1862, p. 12); and it appears to be used at most of the French works where the acid is purified at all. In this case barium sulphate and sulphuretted hydrogen are formed, the latter being in the nascent state, and therefore acting very energetically; this process, has, moreover, the great advantage of leaving nothing soluble behind in the acid. It has been objected that the barium sulphide must be pure and must contain no hyposulphite, since otherwise the well-known decomposition between H_2S and SO_2 and separation of sulphur takes place; this, however, is unfounded, because the barium hyposulphite likewise precipitates the arsenic in the state of sulphide (see below), and only an excess of it (which ought to be avoided in any case) would occasion the above-mentioned reaction.

(*b*) *Sulphide of iron* may be employed in cases where the iron does no harm—for instance, for acid required in the tinning and galvanizing (zinking) of iron &c. Its application, however, is very limited.

(*c*) *Sulphide of sodium* is capable of much wider application, although it, too, introduces a foreign matter (sodium sulphate) into the acid; this, however, is innocuous for most uses of the acid. It can easily be made by reducing sodium sulphate with coal; and it must be added to the acid to be purified until no further precipitation takes place. The filtration of the precipitate will be described hereafter.

(*d*) *Sodium and barium hyposulphites* are very much recommended; the latter is more expensive, but leaves nothing soluble in the acid. The following is the reaction which occurs :—

$$As_2O_3+3S_2O_3Na_2=As_2S_3+3SO_4Na_2.$$

According to W. Thorn (Dingl. Journ. ccxvii. p. 495), the sodium hyposulphite is actually used in some works. Chamber-acid of 106° Tw. is heated to 70°–80° C., and the required quantity of the reagent, either in solution or as powder, is well stirred up with it. The arsenic sulphide is separated in flakes, which soon gather into lumps and sink down to the bottom of the tank; the clear acid is drawn off; and fresh quantities are purified in the same tank, until at last there is too much precipitate collected at the bottom, when it is removed and washed. The operation is very simple; and if an excess of the reagent is avoided, there is very little sulphurous acid evolved. In a particular instance, the average percentage of arsenic in chamber-acid of 106° Tw., before purification, amounted to 0·098 per cent., afterwards to 0·004 per cent. The purified acid contains from 0·03 to 0·04 per cent. sodium sulphate, which for most purposes is harmless. If the contrary should be the case, barium hyposulphite might be used, which is easily obtained by precipitation of sodium hyposulphite with barium chloride; there is then nothing soluble left in the acid.

(*e*) *Precipitation by sulphuretted hydrogen gas.*—This is the process mostly used on the manufacturing scale. We will first give the description published by Schwarzenberg.

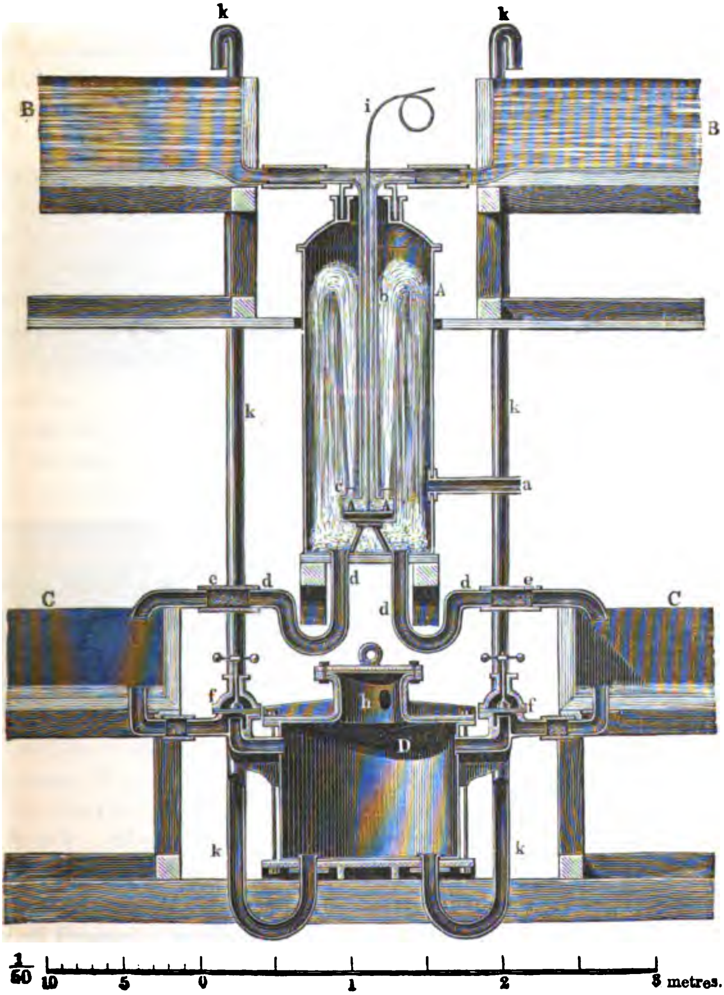
In the German works the sulphuretted hydrogen for the purification of sulphuric acid is obtained as a by-product from arsenical ores. At the Okerhütte in the Harz, where the impure acid, according to Schnedermann, contains, in 10,000 parts, 11 to 14 of arsenious acid and 2 to 5 of lead sulphate along with a little antimony, copper, iron, calcium, and potassium, the following process is used:—

The precipitation of the arsenic with the lead, antimony, and copper is effected in a pan made of sheet lead, 8 feet 2 inches long, 3 feet 7 inches wide, and 1 foot 7½ inches deep, in which the acid, diluted down to 94° Tw., is heated to 75° C. It is thought necessary to dilute down to that degree, because stronger sulphuric acid is itself more easily decomposed by sulphuretted hydrogen. At the bottom of the pan there is a table made of a sheet of lead perforated with many holes, whose edges are turned down all round about 2 inches, so that the table is raised above the bottom of the pan to that extent. This table is 3 feet 7 inches long by 12 inches wide. Below it the lead gas-tube terminates, conveying the sulphuretted hydrogen, which is thus carried into the acid divided into many jets by the perforations of the table. The pan has a lead cover with water lute, provided with a pipe for the escape of the sulphuretted hydrogen in excess; the latter is burnt. The pan contains about 2 tons of vitriol, of which the purification is effected in six hours.

A sign of the arsenic being completely precipitated is, that the acid turns milky. The acid then only contains 0·3 part of arsenic in 10,000 parts; it is allowed to settle, and drawn off into the boiling-down pan by means of a siphon. The brown deposit is placed on an asbestos filter to drain off the acid adhering to it. The sulphuretted hydrogen serving for this operation is made from iron sulphide (obtained by melting together 280 parts of scrap iron and 115 parts of brimstone) and sulphuric acid of 106° and 110° Tw., as the chambers supply it. There are provided for this purpose four cylindrical lead vessels of 14 inches diameter and 18 inches depth. Each of these has in its vaulted cover the lead pipe already mentioned, an opening for introducing the iron sulphide, tightly closed by a screwed-down lid, and an S-shaped lead funnel for pouring in the vitriol. In order to purify the 2 tons of acid in the pan the generating vessels are filled twice, and consume about 3 qrs. 17 lb. of iron sulphide and nearly 1 cwt. of vitriol of 110° Tw. Every three hours the copperas solution produced is run into a pan fixed below the generating vessels, and, after settling, is boiled down to crystallization, scrap iron being placed in the pan in order to saturate the free acid.

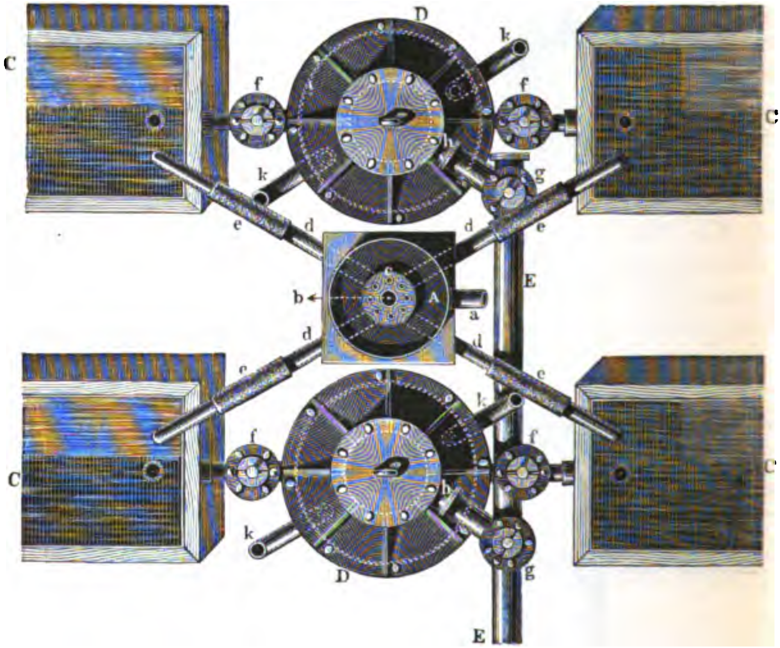
The Freiberg works use an apparatus in which the loss of sulphuretted hydrogen is much less than in the above process. Here it is not thought necessary to dilute the sulphuric acid which is to be treated with sulphuretted hydrogen, probably because it is not heated. Fig. 202 gives a sectional elevation, and fig. 203 a sectional plan, on a scale of 1 : 50, of the precipitation-apparatus. A is the so-called precipitation-tower; it is made of lead, 7 feet 8 inches high and 2 feet 6 inches diameter. The sulphuretted hydrogen gas is conveyed to it by the lead tube *a*, connected with the generating-apparatus. The sulphuric acid to be purified is conveyed, just as it comes from the acid-chambers, into the lead-lined tanks B. These are connected with the lead-pipe *b* in the centre of the precipitation-tower, which at the bottom ends in a low box perforated with eight holes *c*, out of which the acid is squirted in thin jets by means of the hydrostatic pressure acting in the pipe *b*. The minute division produced in this manner con-

Fig. 202.



siderably hastens the precipitation of the arsenic. The squirting-holes can be closed by drawing up the lead-covered iron rod *i*, by which conical points are pressed into them. The purified acid runs off into the lower tanks C by the pipes *d*, which can be stopped by means of pinch-cocks at the interposed india-rubber tubings *e*. From the tanks C the acid is either conveyed into the concentrating-pans, after the arsenic sulphide has settled, or it is run into the forcing-apparatus D, in case it requires another treatment with

Fig. 203.



sulphuretted hydrogen, to be pumped up into B again. For this purpose the india-rubber acid-valves *f*, which can be pressed upon the pipes below by means of screws, are opened. When the vessels D are filled, the valves are closed again, and air, compressed by an air-pump, is forced into D at *h* by means of the pipe E, provided with the valves *g*. The sulphuric acid is then forced through the pipes *k* into the upper tanks. The forcing-apparatus consists of strong iron cylinders completely lined with lead; the valves and other mountings are of "regulus" metal.

Latterly the above-described apparatus has been improved by dividing the acid in the tower, not by a squirting-apparatus, but by hollow horizontal prisms made of lead. The treatment of the acid with sulphuretted hydrogen is repeated a sufficient number of times, till a product is obtained which shows no turbidity when sulphuretted hydrogen is conducted into it, even for some little time. As a rule, three treatments suffice for this. The precipitated arsenic sulphide is allowed to settle completely in large lead-lined tanks; and the clear acid is drawn off by a lead siphon into the tanks from which the concentrating-pans are fed. The precipitate of yellow arsenic sulphide, remaining behind in the settling-tanks, is well washed with water in filtering-boxes lined with lead, and then passed on to the arsenic-works.

The sulphuretted hydrogen at Freiberg is made from a so-called "Rohstein" (coarse metal, matt), produced by smelting raw pyrites, free from blende, with the addition of slags. This matt consists chiefly of sulphide of iron of the composition FeS and Fe_2S; it contains a little silver, which is recovered by the subsequent treatment. It is broken up into pieces of the size of a walnut; and by vitriol from the chambers sulphuretted hydrogen is evolved from it. Formerly the generating-apparatus consisted of several communicating lead vessels provided with a jacket for the circulation of steam; now a single large square lead tank is used for generating the gas. The latter first enters a washing-vessel of lead half filled with water; through two glass windows fixed in opposite sides of this vessel the evolution of the gas can be watched. From this vessel the gas is conveyed direct into the precipitation-tower. The solution produced from the matt is evaporated, with the addition of scrap iron for saturating any free acid; and green copperas is obtained by crystallization. The undissolved residue of the matt is utilized by extracting the copper and silver contained in it.

The details given by Schnedermann are as follows:—

(*a*) Impure acid contained in 10,000 parts—

Specific gravity.	Arsenious acid.	Lead sulphate.
1·832	11·86	3·74
1·837	13·19	2·85
1·836	14·21	5·21

(*b*) After purification, in 10,000 parts—

SO_3	7749·10
H_2O	2243·54
$PbSO_4$ (with traces of $CuSO_4$)	1·72
Na_2SO_4 and K_2SO_4	1·35
$CaSO_4$	0·58
$FeSO_4$	2·91
As_2O_3	0·31
H_2O_3	0·49

It is perfectly free from nitrogen compounds. Subsequently, according to Kerl, acid has been obtained containing no more than 3·15 As_2O_3 and Sb_2O_3 together and 11·28 $PbSO_4$ in 100,000 parts.

A complete description of the older precipitating-apparatus at Oker has been given by Knocke (Dingl. Journ. cliv. p. 185; Wagner's Jahresb. 1859, p. 145).

The more recent precipitating-process used at the Freiberg and a few other works, to which allusion has been made above in Schwarzenberg's description, is described at great length by Bode (Dingl. Journ. ccxiii. p. 25; Wagner's Jahresb. 1874, p. 259); the following is an abstract. According to the former method the vitriol had to be treated three times over before the precipitation was complete, and the evolution of sulphuretted hydrogen from stoneware pots was also very troublesome. When the plant had to be enlarged, the following new arrangements were made :—

1. *Generation of sulphuretted hydrogen.*—For this purpose coarse metal is smelted, consisting principally of FeS, in which at the same time the silver contained in the crude ore is concentrated to the amount of one third of the original weight. The work is done in a blast-furnace with seven tuyeres; the mixture consists of

16·1 per cent. of	lump pyrites, containing on an average 33 per cent. of sulphur.
0·3 „ „	roasted lump pyrites.
0·6 „ „	cinders from subliming arsenic sulphide, with 20 per cent. sulphur on an average.
83·0 „ „	lead slags, with about 30 per cent. silica.
100·0	

Of this mixture 20 to 21¼ tons are daily worked off, with a consumption of 3¾ to 4 tons of coke (19 per cent. of the charge). The yield is 13½ per cent. of the charge as iron sulphide (80 per cent. of the ore); cost of smelting 3*d.* to 3½*d.* per cwt. of the charge. The furnace is minutely described in the original. The coarse metal is broken up into pieces of the size of a fist, and put into the sulphuretted-hydrogen-generators; these receive 4 to 5 tons at a time, which last 8 to 10 weeks. Then weak vitriol of 55° to 77° Tw. is added, such as is obtained in washing the arsenic sulphide; later on, the acid may go down to 32° Tw. Each apparatus daily receives 5 cwt. vitriol of 32° Tw. From 5 tons of coarse metal 7¼ tons of green copperas are obtained, the manufacture of which from the weak lyes takes place in the usual manner. The generators are represented in figs. 204 to 210. They are wooden tanks A and B, made of 3½-inch planks, lined with lead and connected by a lead tube *a*. The tank A (5 feet 6¾ inches square and 5 feet 2 inches deep) is charged with coarse metal after lifting off the cover, or through the man-hole *b*; an india-rubber washer is then put in, and the cover is tightened by thirty screw-bolts. The vitriol is run in through the pipe *c*. B has also a cover, but without an india-rubber joint, as it has only to receive the copperas-liquor forced over by the pressure of the gas in the washing-apparatus (figs. 209 and 210) and the regulating valves, just as is the case with the ordinary laboratory apparatus. The tank A is very strongly bound with iron, which is all leaded over. Steam pipes, *e*, prevent the copperas from crystallizing; *f* serves for running the liquor off. On the bottom of A radially-placed fire-bricks form a grate (fig. 206), upon which a lead sieve *g* is laid; and the coarse metal lies upon the latter. The lateral man-holes *h* permit raking out the residue containing silver. For each 5 tons of chamber-acid, on an average 1½ cwt. of coarse metal is consumed.

2. *Precipitation of the arsenic.*—The chamber-acid of 106° Tw. is treated with H_2S without dilution or heating; the apparatus easily purifies 15 tons of vitriol daily by a single treatment. It is represented in figs. 211 to 217 (p. 478). It consists of a square tower of 5 feet 4 inches × 5 feet 6¾ inches section, and 16 feet 3 inches available height, which is constructed in the well-known manner with a wooden framework and lead sides of 10 lb. to the square foot. The sulphuretted hydrogen enters at the bottom; the air

Fig. 204.

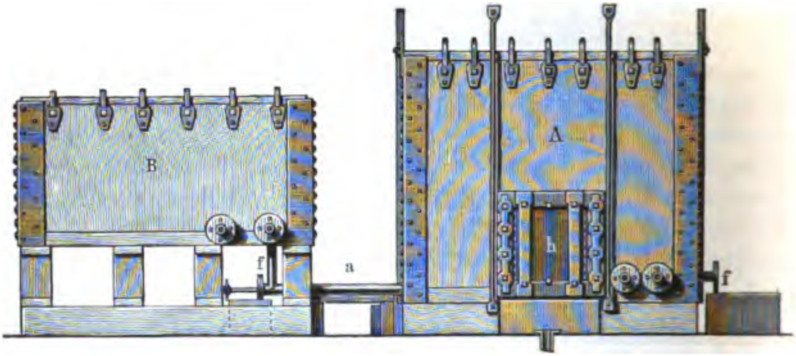


Fig. 205.

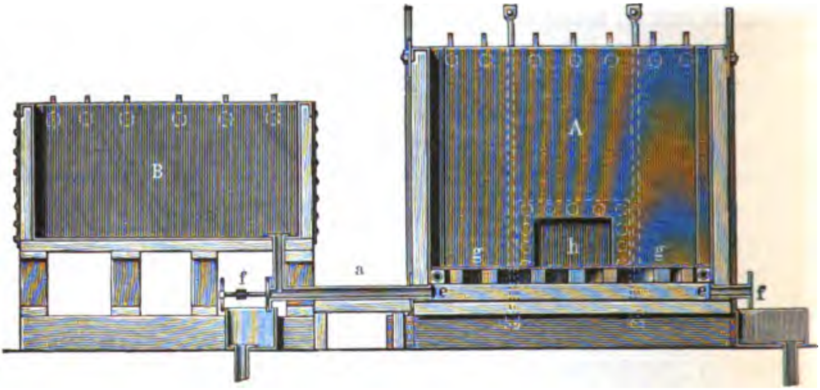


Fig. 206.

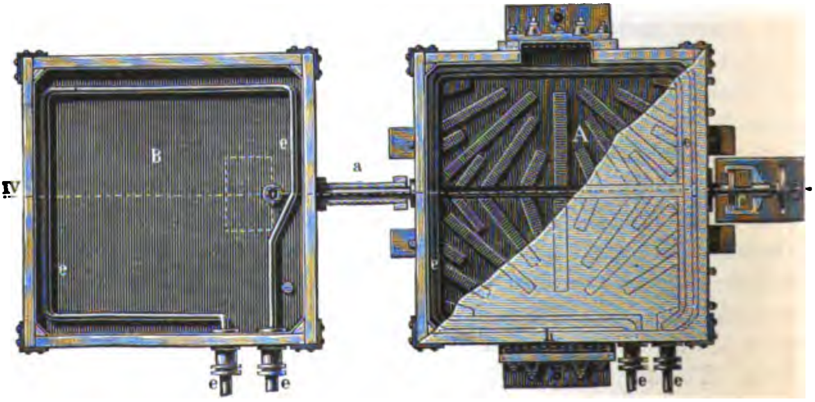


Fig. 207.

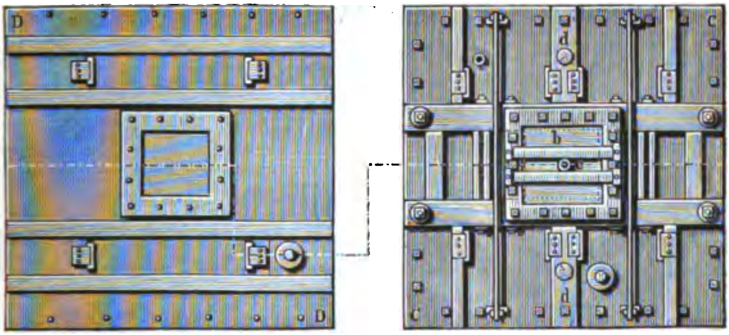


Fig. 208.

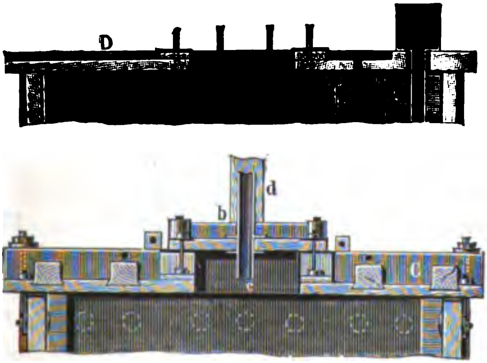


Fig. 209.

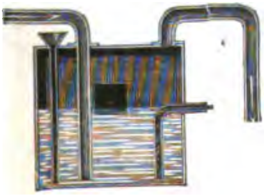
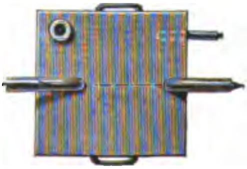


Fig. 210.



carried along with it and the steam escape at the top. The tower is filled with 24 tiers of Λ-shaped inverted lead gutters, 5½ inches

Fig. 211.

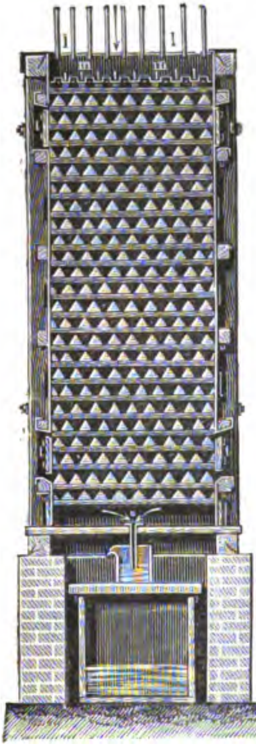


Fig. 212.

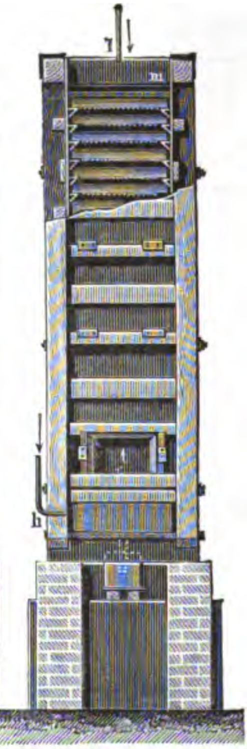


Fig. 213.

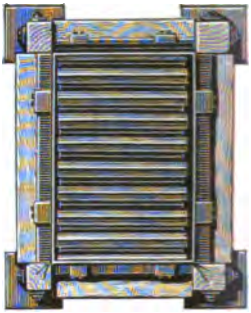


Fig. 214.

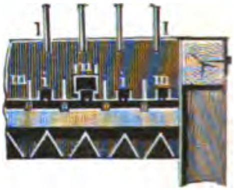
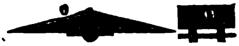


Fig. 215.



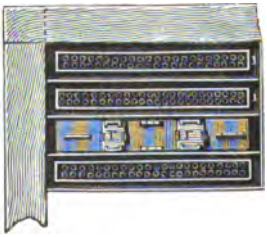


Fig. 217.

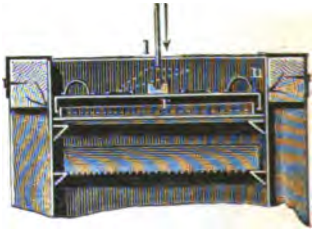


Fig. 216.

high and as wide at the base, made of 10-lb. lead; the lower edges of the gutters have indentations of a tolerably small pattern (fig. 216). Owing to this, the acid cannot run down in jets, but only in single drops, which, in falling upon the next lower gutter, squirt about and present a large surface to the gas. In each tier there are nine gutters, so arranged that the passage between each two of them corresponds to the upper edge of the gutter in the next lower tier. They are 3 feet 3 inches long, and laid loosely on leaded ledges at each side, with 1 inch hold on the latter; their vertical distance is 7 inches; the distance between the tiers, therefore, 1½ inch. The acid runs in at the cover at *l* through nine lead pipes with funnels and regulating cocks, just over each of the lead gutters; there is a hydraulic lute and an oscillating bucket, the details of which are shown in figs. 216 and 217. The lead gutters should not be burnt fast in the tower, as lumps of arsenic sulphide occasionally get jammed between them. These can sometimes be melted and removed by letting in steam.

3. *The filtering and washing of the arsenic sulphide*, in the ordinary way, would be a very troublesome operation. At Freiberg, for this purpose an excellent apparatus is used, which is shown in figs., 218 to 220*. A is the vacuum-retort, B the filtering and washing vessel. The former is a small, worn-out steam-boiler of 1 foot 10 inches diameter and 5 feet 7 inches length. Steam is conveyed into it through *a* from a boiler; through *b* the air goes away along with the condensed water; and the cock there is only shut when steam has passed through for several minutes. Then *b*, and afterwards *a*, are shut, and the boiler is allowed to cool for some time in order to condense the steam. Then the cock *c* is opened, which connects the vacuum-retort and the space below the filtering-layer in the box B. This box has already been filled with the acid to be filtered, whose level is always kept at the same height, lest any cracks be formed in the exposed layer of arsenic sulphide, through which air would enter and destroy the vacuum. By several times shutting *c*, opening *a* and *b*, driving out the air by steam and cooling down the boiler A, a vacuum of from 10 to 12½ lb. may be obtained. [Probably less steam and labour would be expended if an air-pump were used, as is done in England.] The same vacuum-retort [or air-pump] may work several filters, which may be filled, washed, &c. at will, since the cock *c* permits isolating every one of them.

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* Precisely the same principle has been applied in England for many years past for filtering the lime-mud in causticizing and for many other purposes.

The filters B are made of 2-inch planks, strengthened at the bottom at *e*, fig. 220, lined with lead, 4 feet 4 inches × 5 feet 7 inches section and 1 foot 10 inches high. A double pavement of acid-proof fire-bricks leaves a gutter, communicating with the burnt-on pipe *l*. This ends in an intermediate vessel C, whose cover is provided with connecting-tubes for the pressure-gauge, *o*, and the vacuum-retort, A, at *c*; *m* takes the acid to the receiving-tank *n*; but the pipe *mn* must be longer than the height of a column of

Fig. 218.

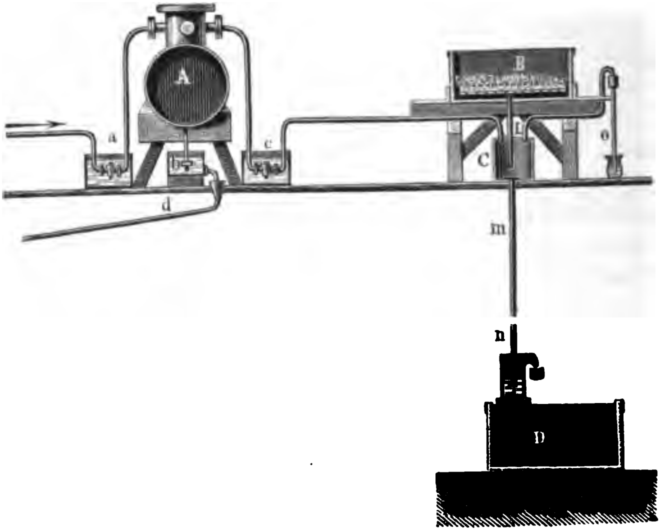


Fig. 219.

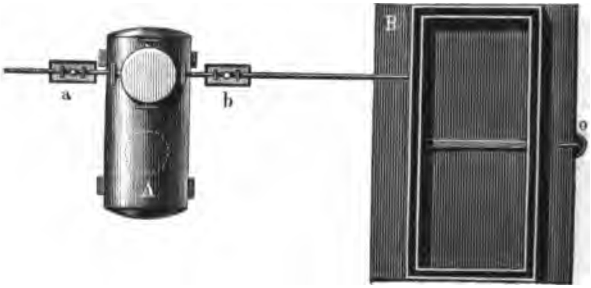
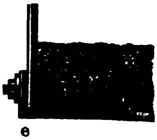


Fig. 220.



water forced up by the atmospheric pressure, lest the acid should get over into *c*. Over the fire-bricks in B there is a layer *n* of broken-up quartz (fig. 220)—at the bottom, pieces of the size of a walnut—higher up, finer grain; over this there is a finely perforated sheet of lead, and on the top a layer of powdered arsenic sulphide; the whole filtering-stratum rises 11½ inches above the bottom of the vessel. Where the acid runs in, a piece of lead is placed so as to keep the top layer from being damaged. Every two or three weeks the layers *n* and *m* and the perforated lead plate must be taken out, and the quartz pieces as well as the arsenic sulphide must be rinsed in water. The whole plant requires several pressure-apparatus (acid-eggs) and a good air-pump.

At Oker the work is done very much as at Freiberg (Bräuning, p. 142); but here only that portion of the acid is purified which is not sold to large consumers, especially for superphosphate-making. It is thought best here to dilute the acid to 97°–100° Tw., and to assist the generation of sulphuretted hydrogen by injecting steam at the beginning.

An English patent of M'Kechnie and Gentles (No. 3229, 25th August, 1877) contains essentially the same process as is practised at Freiberg and Oker.

Purification of the Sulphuric Acid from Nitrogen Compounds.

Already, when treating of the purification of vitriol from arsenic, it has been stated that mostly at the same time the nitrogen compounds are removed, and always when sulphuretted hydrogen is employed for that purpose. In most works, it is true, no such purification from arsenic takes place; but for most uses of the vitriol the small proportion of nitrogen compounds which they contain is so unimportant that their removal is not called for. In all cases, however, where sulphuric acid has to be concentrated in platinum apparatus, it must be purified as much as possible from absorbed nitrogen acids, as otherwise the platinum, as we shall see hereafter, would be much more strongly acted upon. Since this has been known, probably such purification takes place nearly everywhere, but by different methods.

1. *Purification by sulphurous acid.*—Payen has proposed a contrivance for this object, which is also found in the diagram of the acid-concentration in lead and platinum to be given hereafter from Schwarzenberg's work. This is a cover over the first boiling-down

pan with partitions which force the gas to travel twice backwards and forwards, and below which the sulphurous kiln-gas circulates. Some, instead of this, use pans arched over. This apparatus, however, fulfils its purpose very inefficiently, because the contact between the vitriol and the sulphurous acid is very incomplete. This object can be attained perfectly in all works where a Glover tower is employed; in this the acid can be fully denitrated, and, moreover, some little sulphurous acid can be dissolved, in which case, as Scheurer-Kestner has shown (see below), it acts least upon platinum; but, unfortunately, the Glover-tower acid, owing to its large percentage of iron, cannot well be used for concentration in platinum stills.

2. *Treatment with brimstone* has been proposed by Barruel. It is used in the shape of flowers of sulphur, which sometimes, according to Schwarzenberg, is put into boxes of stoneware, placed in the first pan, in which the temperature does not rise to the melting-point of sulphur, and in which the vitriol contains most water. Special care must be taken that no sulphur gets into the following pans, because strong hot vitriol is decomposed by sulphur with the formation of SO_2, and for each part of S 6⅛ parts of SO_4H_2 are lost. According to Bode ('Gloverthurm,' p. 3) this process is not efficient; so long as the brimstone is still in the state ot powder, its action is very small, while the lead is already being acted upon by the nitrogen acids. Later on, with the rise of temperature, the brimstone melts and rises in small drops to the surface of the hot acid, whence it mostly escapes into the air as SO_2.

3. *The employment of organic substances.*—*Oxalic acid,* proposed by Löwe, has already been mentioned in the purification from arsenic. *Sugar* has been proposed by Wackenroder. Skey recommends agitation with *charcoal,* but only for dilute acid (Chem. News, xiv. p. 217). Olivier uses a little alcohol in the lead pans ('Rapports du Jury international,' 1867, vii. p. 35).

None of these substances is used to any extent in manufacturing practice.

4. *Ammonium sulphate* has been proposed with this object by Pelouze (Ann. Chim. Phys. lxxvii. p. 52), and has been proved to be the best of all. By this the nitrogen acids can be so completely removed that the vitriol is tinted red by the first drop of a solution of potassium permanganate. In this case nitrogen escapes, according to the following equations :—

$$N_2O_3+2NH_3 = 3H_2O+4N,$$
$$3NO_2+4NH_3 = 6H_2O+7N,$$
$$3NO_3H+5NH_3 = 9H_2O+8N.$$

This means is now universally employed, unless the acid has been sufficiently denitrated in the Glover tower. Under normal conditions 0·1 to 0·5 lb. suffice for purifying 100 lb. of vitriol.

Production of chemically pure Sulphuric Acid.

Hayes (Dingl. Journ. cx. p. 104) has proposed to add nitre to the vitriol of 152° Tw., coming from the lead pans, sufficient for destroying the largest portion of any hydrochloric acid present, and for oxidizing completely the sulphurous and arsenious acids, then to destroy the nitrous acid &c. again by adding ⅓ per cent. of ammonium sulphate—to add a little oxide of lead, to cool and settle in leaden vessels, and to cool the clear acid siphoned off in shallow lead pans down to −18° C. In this case the hydrate $SO_4H_2+H_2O$ crystallizes out; the mother-liquor containing all impurities is decanted; the crystals are washed with pure acid, and then form square prisms sometimes an inch thick and 1¼ in. long. These are fused in clean lead vessels, and used as they are, or further concentrated in a platinum still. This process was intended to save the distillation; it has not been successful, however; for it is troublesome and yet does not produce a really pure acid.

The only plan for making perfectly pure sulphuric acid for pharmaceutical and analytical purposes is still *fractional distillation*, connected with such operations as previously remove the volatile impurities of the vitriol or convert them into fixed compounds. We have seen above how the arsenic and the nitrogen compounds can be removed. It is best to destroy the latter first by ammonium sulphate, and to convert the arsenious acid into non-volatile arsenic acid. It is safer, on account of the danger of spurting, first to remove both nitrogen compounds and arsenic by means of sulphuretted hydrogen; but then the acid must be much diluted previously. It never becomes absolutely free from arsenic in this way; it is therefore always preferable to employ brimstone-acid for rectification.

According to Nicklès, *hydrofluoric acid* is sometimes found in vitriol; and it can be removed by diluting it with twice its bulk of water and heating it for 15 hours.

The fixed substances, such as iron, lead, copper, &c., remain in the retort on rectifying; and in order to avoid contamination with organic substances, the receiver is changed when about $\frac{1}{20}$ part of the acid has come over; the distillation is interrupted when only $\frac{1}{8}$ to $\frac{1}{10}$ of the acid is left behind. The portion distilling between these two limits is quite pure.

The distillation of sulphuric acid is a very disagreeable and even dangerous operation, on account of the strong *bumping* caused by the sudden development of large bubbles of vapour; this is especially favoured by the lead sulphate separating. In such cases the retort is sometimes bodily lifted up, and of course smashed when it falls back upon its seat. The bumping must therefore be avoided as much as possible, for which purpose the following plans have been proposed.

Berzelius prescribed heating the retort more from the sides than from below, by placing a sufficiently wide sheet-iron cylinder upon the grate of the furnace, so that the bottom of the retort just fits into it; the coals in the furnace then only heat its sides. In this case, however, the iron cylinder may act as a cracking ring; and A. Müller (Polyt. Centralbl. 1860, p. 1069) therefore employs an iron boiler, in whose bottom a special iron ring protects the retort-bottom from heating, whilst the remaining space of the boiler round the retort is filled with fine cast-iron borings. In any case the retort ought to be heated in a cupel just fitting it, which is generally filled with sand; Reese (Dingl. Journ. clv. p. 395) puts ashes on the bottom, as a bad conductor of heat. Frequently, however, the retort is heated direct in a fire, and is merely protected by asbestos or by a paste of clay which is continued up to the curve of the neck, so that the vapour is prevented from condensing too soon.

In any case the retorts must be made of very good glass, free from knots, equally thick all over, and not too large; the neck must be protected against draughts, and must not extend to the middle of the receiver, as the latter might be cracked by the hot drops of acid falling into it. It is neither necessary nor advisable to cement the joint between the retort and the receiver, or to cool the latter, considering the high boiling-point of the acids; but it is useful to place a strip of asbestos between the neck of the retort and the receiver, in order to protect the latter against overheating at the point of contact.

The bumping is very commonly avoided by putting in substances which favour a regular evolution of vapour. For this purpose the following are useful:—platinum scraps or wire, for instance in the shape of spirals; bits of quartz, of porcelain, or of very hard coke. Pelloggio recommended a wide glass tube, drawn out to a fine point at the lower end, and reaching almost down to the bottom of the retort; through this the air can communicate with the interior (Polyt. Centralblatt. 1868, p. 392). Hager has tried this and found it useless. Dittmar conducts a continuous slow current of air through the boiling acid (see above, p. 19).

When distilling about 1 cwt. at a time, it takes from 5 to 6 hours of moderately strong heating before the contents of the retort begin to boil; after 12 hours one twentieth has distilled off. The receiver is now changed; after 36 hours (counting from the commencement) the acid is distilled off within one eighth or one tenth, and the operation is stopped. According to whether the first change of receiver has been made a little sooner or later, acid more or less concentrated is obtained.

The following method is very much to be recommended, because the danger of handling such large quantities is hereby avoided. A small tubulated retort holding from a pint to a quart is employed; above this, a little to one side, a bottle of convenient size is mounted, provided with a glass cock, into which the sulphuric acid to be rectified is put, after it has been freed from all volatile impurities by previous heating. The distillation is now started in the small retort, which is about half filled, and into which a few scraps of platinum are put. Afterwards, by means of the glass cock and of a finely drawn-out glass tube, as much acid is allowed to run continuously from the stock-bottle into the retort as is distilling off. The operation may be continued till too much of fixed substances is accumulated in the retort. The author has seen this plan at work in English factories.

CHAPTER XIII.

THE CONCENTRATION OF SULPHURIC ACID.

The vitriol, as obtained direct in the chambers (that is to say, from 106° to at most 124° Tw. strong), is sufficiently concentrated for many technical purposes; and where the acid is used up again for such purposes at the same works, its further concentration is, of course, out of the question. This is the case, for instance, with large industries having their own vitriol-works, with the manufacturers of superphosphate and of sulphate of alumina (concentrated alum). Even for making sulphate of soda from common salt it is quite easy to manage with acid of 124° Tw., although stronger acid is better; and in fact some alkali-makers (not so many now as formerly) work without any concentrating-apparatus, making their chamber-acid as strong as possible. This, to be sure, excludes the application of a Gay-Lussac tower; and such works certainly did not possess such a tower. With the introduction of the Glover tower the state of matters was changed, inasmuch the manufacturers using this tower can concentrate all their acid to 144° or or even 152° Tw. without any cost, and thus arrive at the same point as those who, not using that tower, concentrate their acid in lead pans. But since Glover towers are far from universal, and since they are not suitable for all the uses of sulphuric acid (see p. 441), we must here describe the other concentrating-apparatus as well. These come into use especially where vitriol of 170° Tw. is to be made, for which the Glover-tower acid is not very well adapted.

It should be borne in mind that in boiling dilute sulphuric acid the escaping vapour consists almost entirely of water, and contains very little sulphuric acid indeed. The acid remaining behind will therefore become more and more concentrated, without any material loss of acid, so long as 144° Tw. is not exceeded. Walter (as quoted in Bode's 'Glover Tower,' p. 17) found that the loss in concentrating vitriol in open pans up to 144° Tw. only amounts to 0·01 per cent. At the same time the boiling-point, which in the case of chamber-acid is about 147° C., gradually rises: that of acid of 144° Tw. is 200°; that of acid of 152° Tw., 215°. Beyond this the boiling-point rises very rapidly, and finally becomes stationary at 338° C., at which point not yet real sulphuric acid (SO_4H_2), but an acid containing about 1·2 to 1·5 per cent. of water remains behind. In practice this limit is hardly ever reached; the heating is stopped when the remaining acid nominally shows 170° Tw.; for the most part its real density amounts to only 1·830 or 1·835 = 166° or 167° Tw. A table of the boiling-points of sulphuric acids, according to their dilution, has been given above at p. 36.

The way in which sulphuric acid is to be concentrated is modified, first, by the *material of the concentrating vessels.* From what has been said above (p. 40) it follows that sulphuric acid of 144°, or even up to 152° Tw., acts very little upon the lead, even when hot; and so long as the acid has not to be stronger than 144° Tw., *leaden vessels* are always used*, which offer the advantage that they can be made of any size, and that, when they are worn out, they can be very easily melted up and the material used over again. It is not advisable to carry on the concentration in lead above 144° Tw., because at that point the lead is much acted upon; and in no case can lead pans be used beyond 152° Tw., both because in that case the boiling-point of the acid too nearly approaches the temperature at which the lead begins to soften, and because the acid then acts too strongly upon it.

The further concentration of the acid must take place in vessels of ~~lead~~ or platinum, or in apparatus of peculiar construction, which will be described hereafter.

glass

The concentration of sulphuric acid to 144° *or to* 152° Tw. is therefore always carried on in *lead pans* (apart from the Glover tower). These pans, however, may be constructed in very different ways. They may either be heated by a direct fire, and either from the top or from the bottom, or by steam, or by the waste heat of the pyrites-burners; and their construction differs accordingly, as will appear from the detailed description.

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* The only exception is a process of Faure and Kessler's, hardly much in use, of carrying on even the *first* concentration up to 144° Tw. in platinum dishes.

I. *Lead pans heated from the top.*

This is the appropriate mode of firing when the purity and especially the appearance of the vitriol are of less moment than a saving in fuel and the accomplishment of a large amount of work. The acid in this case is, of course, contaminated by the flue-dust, and is always more or less stained by sooty matters, whence its English name, "brown vitriol," has arisen. These contaminations are quite harmless when it has to be used for decomposing salt, for superphosphate, and for many other purposes.

On the other hand the rate of evaporation with a fire from above is very quick, because, first, the hot gas is brought into immediate contact with, and thus can communicate its heat much better to, the acid than when the two are separated by metallic plates; secondly, the vapours formed thereby are at once removed by the draught—which, as is well known by experience, very much assists the evaporation. Moreover, fired from the top, the pans, if properly constructed, are much less acted upon than when fired from below; especially the danger of being burnt through from the workmen's carelessness is much smaller.

Concerning the loss of acid in evaporation no experiments have been published; probably it is somewhat larger than with pans heated from below. Hasenclever ('Berichte d. deutsch. Chem. Gesellsch.' v. p. 504) mentions that these "evaporating-furnaces" have been done away with again at many works because the acid is easily overheated, and because much acid may escape with the fire-gas. In England, where the pans with top heat have been built in a more suitable manner than those mentioned by Hasenclever, they have never had to be removed for the reason mentioned by him.

According to the above, pans with top-heat are especially suitable for larger alkali- and manure-works or for acid to be sold to the latter, but less so for sale-acid for other purposes. They were far more extensively used in England than pans with bottom-heat; but they have become superfluous wherever there are Glover towers. Such pans have been described by Godin ('Annales des Mines,' 1865, p. 344) and by the author (Dingl. Journ. cci. p. 352). In any case the lead must be protected from direct contact with the fire; or at least the pans must be cooled in such a manner that the lead cannot melt. The first way of doing this is to keep the pan always filled to the same level, and that near to its top, leaving only a sufficient margin to prevent any boiling-over. And in ordinary work the acid is never drawn off altogether unless for repairs; but, the concentrated acid being heavier and sinking, it is continually drawn off from the bottom, and fresh acid is continually run in at the top, as long as the concentrating process goes on. Even then the empty portion of the pan has to be protected, especially at the fire-bridge; and, in many English works, for this purpose a lead pipe was burnt on all round, through which ran a continuous stream of cold water. This contrivance cannot be highly recommended, because the pipe soon gets leaky. Moreover the raising of the water costs something; and therefore the following arrangement is preferable.

Fig. 223 shows a front elevation, fig. 222 a cross section, and fig. 221 a plan, of a pan with top heat. The fireplace, A (2 ft. × 4 ft.),

Fig. 221.

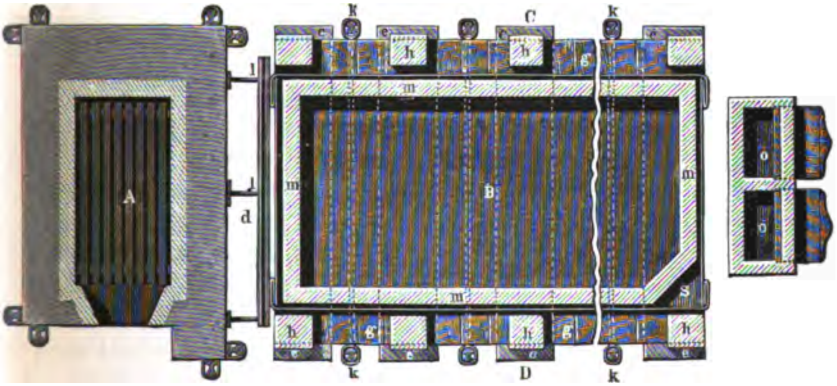


Fig. 222.

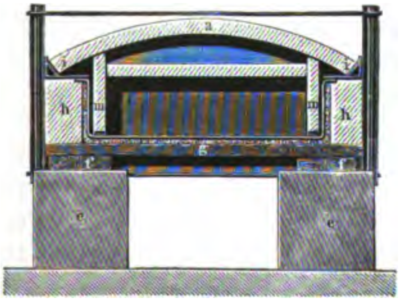
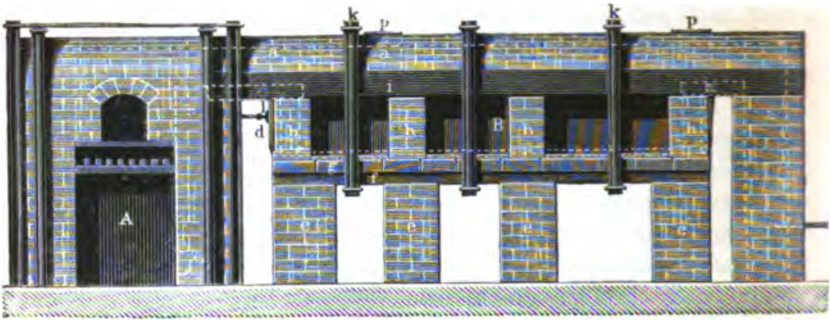


Fig. 223.

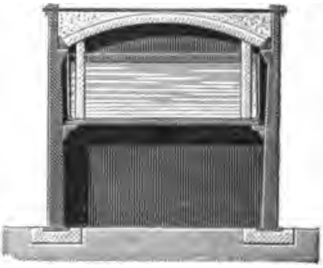


is built up quite independently; its only connexion with the pan B is by the arch *a*, and the fireclay slabs *c*, 2 feet long, lying on the fire-bridge, *b*; the slabs *c* have a 6-inch hold on *b*; and as the space *d* between A and B is 1 foot wide, they project 6 inches into B. The grate in A is here shown as a plain one; it might, of course, be more rationally constructed; and at some works it was replaced by a generator fire. Anyhow the air-channel, *d*, prevents any injurious influence of the heat of the fireplace on the pan, and we need only heed the flame itself.

The pan B is always made of a single sheet of lead, weighing from 15 to as much as 30 lb. per superficial foot; the corners are not made by cutting out, but by folding over, as shown plainly in fig. 221. Since such stout lead cannot easily be bent cold, along the line marked out for the folding a small fire of shavings is made, of course taking care to avoid melting the lead; the lead then softens sufficiently to be bent with ease. The pan is placed on brick pillars, *e e*, standing quite free, so that the space between them and below the pan is accessible at any time. On the pillars strong wood beams, *f f*, are laid; and across these 3-inch planks are placed close together; they are covered with a thin layer of sand, on which the pan itself is set. The pillars and beams project on each side 10 inches beyond the pan itself, and thus support small brick pillars, *h h*, 9 inches square, not quite touching the lead, and connected together at the top by cast-iron girders, *i i*. These have an angular section, and serve as springers for the arch *a*, which is thus quite independent of the pan. To be sure, the pillars, *h h*, are much too weak to bear the side pressure of the arch; but this is kept up by the binding-rods, *k k*. The upper margin of the lead pan is bent round at a right angle, and jammed in between the pillars, *h h*, and the girders, *i i*; in this way the sides of the pan are kept stiff. Next to the fireplace, where the pan becomes hottest and most readily gives way, it may be protected by iron rails and stays, *l l*.

A neater, but rather dearer, plan is this:—Instead of the brick pillars, *e e*, there are cast-iron columns provided, carrying, about halfway up, brackets, upon which metal plates for supporting the pan-bottom are laid. The columns are connected at the top by metal girders serving as springers for the pan-arch, and are kept together by bracing-rods. Fig. 224 will make this plainer.

Fig. 224.



The proper protection of the pan from the fire is brought about by the dry wall, *m m*, built up all round within the pan, of the best, hardest, acid-proof firebricks or stoneware slabs. At the long sides this wall reaches up to the arch; at the fire-end it only reaches to the upper margin of the pan, and there carries the projecting fireclay slabs, *c*; at the chimney-end there are similar slabs, *n*, reaching up to the down-draught, *o*. The wall, *m m*, stands about 1 inch off the pan-sides, and has openings at the bottom, so that the acid can circulate freely. It is evident that the fire can nowhere touch the lead itself; and, moreover, the pan is also protected outside by the cooling action of the air; so that it cannot possibly melt, or even soften. The greatest danger of this is still left at the fire-end, to which, certainly, great attention must be paid. In the arch there are manholes, *p p*, and an inlet-pipe for acid, whilst the strong acid is drawn off by a siphon from the end *s*, left free by the arch; it is still better to attach to the bottom of the pan an overflow-pipe which rises to its top, and whose mouth can easily be narrowed according to requirement. The pan is preserved better if the fresh, cool acid runs in at the part nearest the fire-bridge whilst the strong acid is taken away from the opposite end of the pan, where it is coolest. It is always too hot to be used directly; and therefore it is run into shallow lead coolers, stayed by iron or wood frames, of which one is being filled whilst the contents of the other are being used. If the acid should not run off sufficiently strong, either the fire is increased, or the supply of weak acid is diminished, or both.

The width of the pan is dependent upon that of the sheet-lead; if for the sides about 17 inches each are allowed, about 4 feet 11 inches generally remain. The length is always much more considerable, rarely below 20 feet, but sometimes as much as 33 feet. The longer the pan, the better the fire is utilized. The consumption of fuel is always much less than for pans with bottom-fires; Bode estimates it at from 10 to 12 per cent. of the strong acid, but without any experience of his own. The repairs of a properly constructed pan of this kind are much less than those of a pan with bottom-heat (as it always is in analogous cases); and the work done is much larger for an equal area. A pan of 4 feet 11 inches width by 33 feet length was sufficient, in the author's experience, for boiling down 80 tons of acid of 144° Tw. per week, from chamber-acid of 116–124° Tw.

Clough ('American Patent, Official Report,' i. p. 495, iii. p. 166) has proposed a similar apparatus for cencentrating the vitriol up to 170° Tw. His pan was protected from the fire, inside by a wall, and outside by cold water contained in an iron jacket. This can hardly be put into practice, because the loss of acid vapours would be too great.

2. *Lead pans with bottom-heat.*

These pans are mostly made of much smaller size than those with top-heat; the essential reason of this is the different wear and tear which they suffer according to whether they are more or less exposed to the fire; moreover the concentration in this case is very regular, the pans always being arranged in sets, so that the weak acid flows in at one end of the set and runs over from one pan to another till it runs off sufficiently strong at the other end of the set, in order to be used up or sold, or to be further concentrated in platinum vessels. Sometimes, however, long pans made in one piece are used, especially in England. In that case the first part, nearest the fire, is protected by an arch, the larger part of the pan-bottom behind this by fire-clay slabs or metal plates, as shown in figs. 225 to 227.

The latter are sometimes covered by a thin layer of sand, in order to communicate the heat evenly to the pan; but this greatly

Fig. 225.

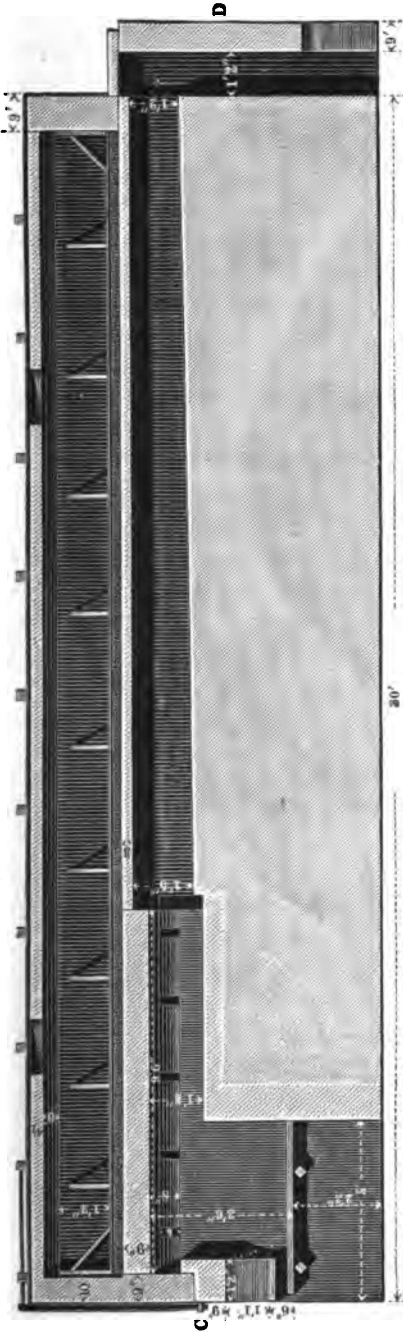
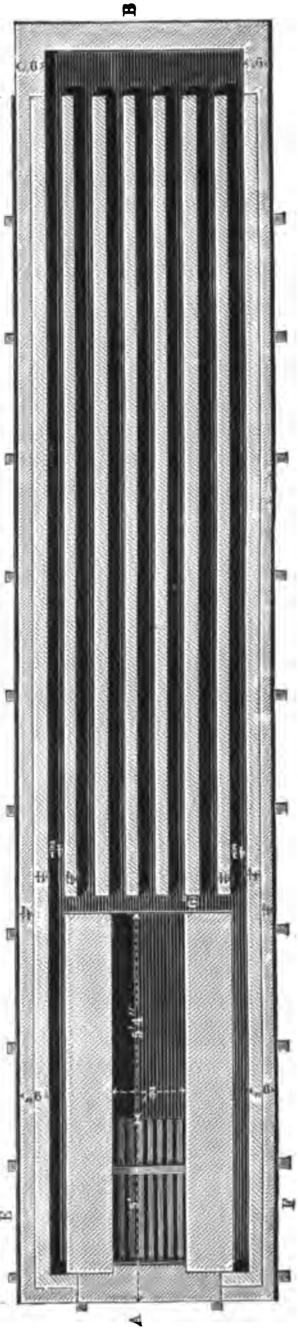
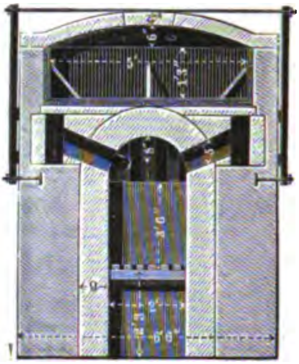


Fig. 226.



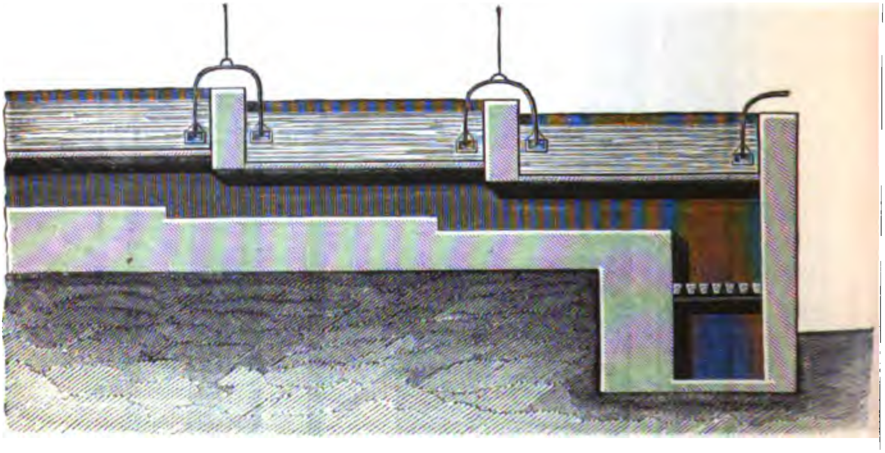
hinders the heat-convection. The pan is stiffened inside by iron stays covered with lead; and it is covered by an arch to carry off the vapours into the open air or into the chambers—the latter rarely.

Fig. 227.



On the Continent small pans are very generally used, of 5 to 7 feet length and width, and from 12 to 16 inches depth, of which from four to six form a set. They are made of 15- to 18-lb. lead, mostly by bending up the sides and folding over (not cutting out) the corners. They are often set in steps, each pan about 2½ inches lower than the preceding one, as shown in fig. 228; in other cases,

Fig. 228.



however, they are placed at one level, but are made of different depths—the pan which receives the weak acid being the deepest (16 inches), and each following one a little lower, the last pan (for strong acid) coming down to 12 inches. In this way the acid can also flow from one end of the set to the other; and this arrangement will be shown hereafter, in the section on concentration in platinum dishes. At the Oker Works there is a long pan divided by partitions into seven compartments of equal height and level; the fire-grate is in the centre of one side; and the flame first passes in the centre to the back, and then returns at both sides to the front of the pan.

The acid is generally carried over from one pan into the next by continuously acting cup-siphons, as seen in fig. 228. But as such siphons frequently cease to act in consequence of air getting in owing to the slow current and the small difference of levels, there ought always to be an overflow-pipe provided to prevent the pans from running over. It is even preferable to replace the siphons altogether by overflow-pipes, which take the acid from the bottom of one pan and allow it to run on to the top of the next one; this arrangement certainly requires the work of a very good plumber, to last without continual repairs. The chamber-acid is constantly running into the first pan in a regulated stream; and the strong acid runs off from the last pan without any further interference, the supply being so regulated that the proper strength is obtained.

The pans are always stayed and protected from the direct action of the fire by cast-iron plates, which are thicker at the fire end than further off—say, decreasing from 2 inches down to $\frac{3}{4}$ inch. Frequently the first pan, below which the fireplace itself is built, is protected by an arch.

Opinions differ on the point, in what way the firing of the pans should be arranged. In most places there is the decidedly rational arrangement of putting the fireplace under the strong pan, and allowing the fire to travel towards the weak pan, which receives it last of all. In this case the greatest heat exists where it is most required, since the concentration of the strong acid is more difficult and its boiling-point higher, and since the fire-gas ultimately comes into contact with cold acid. When the pans are set terrace-fashion, the fire takes its most natural direction, viz. upwards. Still in some places the opposite arrangement has been introduced—placing the fire under the weak pan, the flame travelling towards the strong pan. No doubt this is done with the intention of protecting the strong pan from being worn out too soon, which, however, can be done in other ways just as well. At least in some works the arrangement first described has been exchanged for that last described, because, it was said, the strong pan suffered too much; but the author has generally received information to the contrary.

Bode cites the temperature and strength of the acid in a set of six pans, where the fire travelled in the same direction as the acid, viz.:—

Acid running in.	1st pan.	2nd pan.	3rd pan.	4th pan.	5th pan.	6th pan.
	°	°	°	°	°	°
a. Temperature 25°......	112	150	160	148	145	143 C.
Strength 110°	113	120	128	134	140	144 Tw.
b. Temperature 24°......	110	145	156	145	142	142 C.
Strength 110°	113	118	126	134	140	144 Tw.

Here the hottest pan is the third; so that the fire is badly utilized. According to his experience this set required 20 parts and upwards of coal to produce 100 parts of acid of 144° Tw.; whilst in the set figured below, where the fire meets the acid, only 15 to 16 parts of coal were used (on the average of several years). For each ton of strong acid, in 24 hours about 20 superficial feet of pan-bottom may be reckoned; the whole set, therefore, furnishes 6½ tons every 24 hours.

Bode gives the temperatures and strengths of the acid during concentration in pans with the proper style of setting as follows:—

Set of four pans:

Acid running in.	1st pan.	2nd pan.	3rd pan.	4th pan.
	°	°	°	°
Temperature 20°..................	52	78	120	138 C.
Strength 106°	...	...	...	144 Tw.

Set of three pans heated by the pyrites-burners:

Acid running in (heated previously).	1st pan.	2nd pan.	3rd pan.
	°	°	°
Temperature 70°.....................	105	128	147 C.
„ 57°.....................	92	106	125 C.
Strength 106°	...	...	144 Tw.

According to Hasenclever, it is well to regulate the working of the pans by thermometers, in order to avoid any risk of damaging them.

Figs. 229 to 232 represent the set of pans designed and constructed by Bode, where the fireplace is outside, in order to save the

Fig. 229.

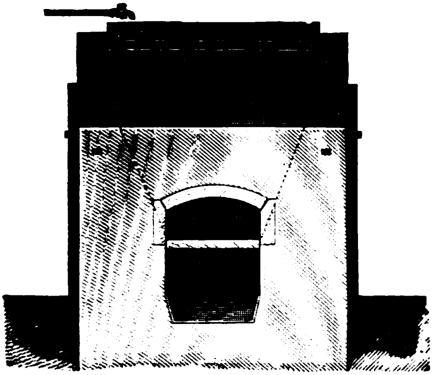


Fig. 230.

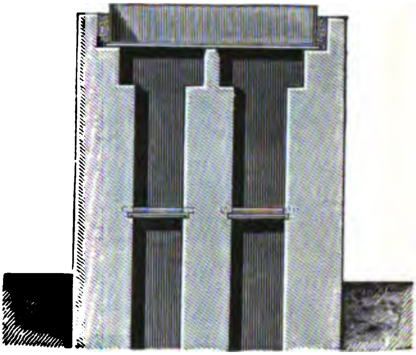


Fig. 231.

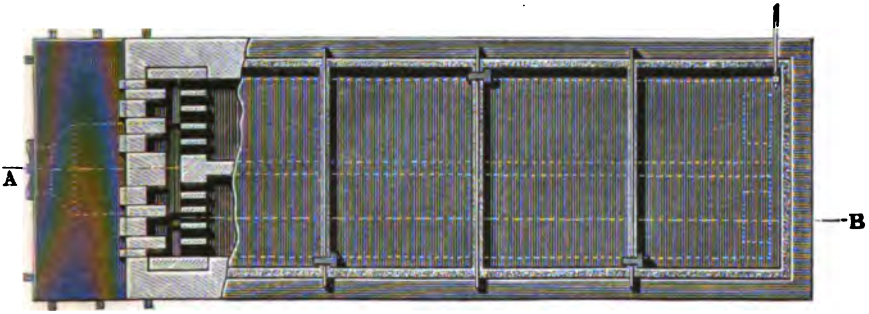
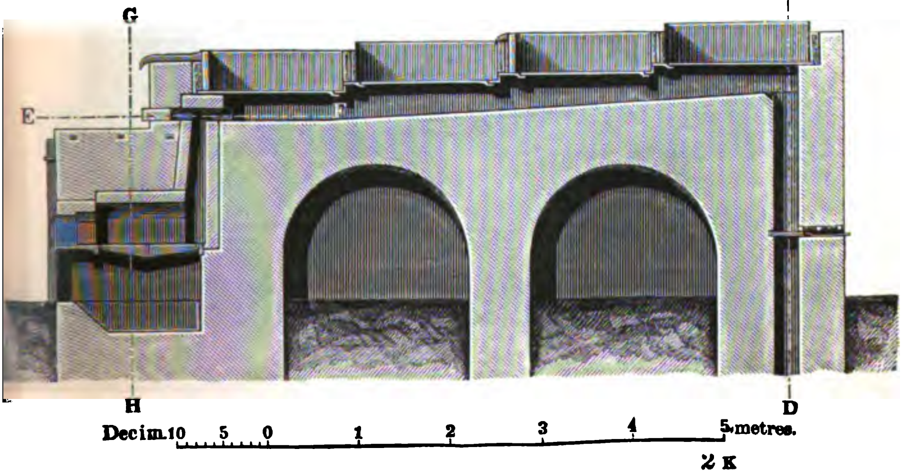


Fig. 232.



first pan. The second plan designed by Bode, and represented in figs. 233 to 236, seems still better. In this there is no outside fireplace, but a protecting arch. From this, by means of a pan-area of 118 superficial feet and a fire-grate of 6½ superficial feet, 5 tons

Fig. 233.

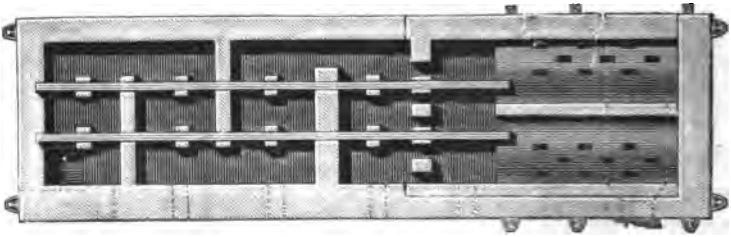


Fig. 234.

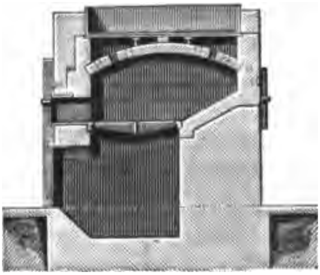


Fig. 235.

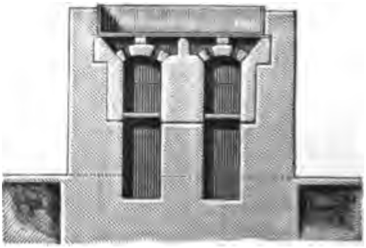
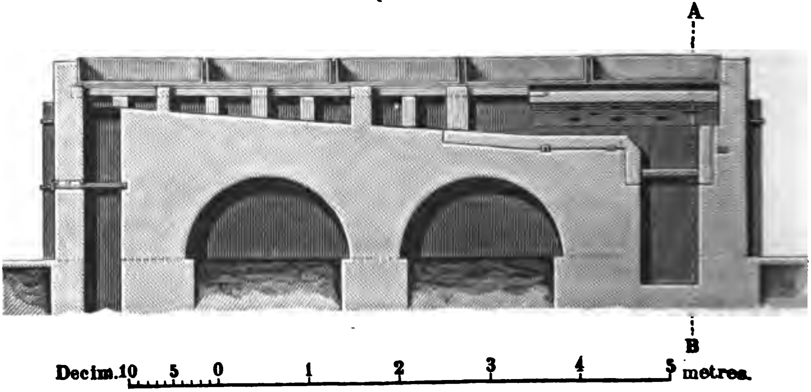


Fig. 236.



of strong acid could be produced every 24 hours, with a consumption of 12 to 14 per cent. of Silesian coal. Figs. 233 and 235 show a modification, in which a Fairbairn's double fireplace is used.

According to Scheurer-Kestner (Wurtz, 'Diction. de Chimie,' iii. p. 159), four pans, 6 feet 6½ inches by 3 feet 11 inches each, permit the concentration from 109° to 152° Tw. of sufficient acid to produce 3 tons of concentrated acid daily, with a consumption of no more than half a ton of coals.

Bode calculates the cost of erecting a concentrating-apparatus like that shown in figs. 233 to 236 at £150, and that of keeping it in good working order at 12 per cent. per annum. The cost of the concentration itself, reckoning coals, wages, and wear and tear, in four actual cases, amounted to from *2s.* *3½d.* to *2s.* *8d.* per ton.

3. *Lead pans fired by waste heat.*

If in a factory there are platinum apparatus for making acid of 170° Tw., the fire of these can never be so far utilized that the waste heat could not be employed for heating lead pans; and how this is actually done is shown in the drawing to be given further on.

Much more generally applicable, and quantitatively more efficient, is the utilization of the waste heat of pyrites- or sulphur-burners for concentrating chamber-acid. Where there is no Glover tower (which utilizes that waste heat in a different and certainly even more advantageous manner) the above process is most rational, since here also the same operation that produces the concentration of the acid, fulfils another useful function, that of cooling the burner-gas before it enters the chambers.

The pans used here are generally made exactly like those for concentrating with bottom-fires. They are mostly placed on the pyrites-burners themselves; they must not, however, be set directly upon the burning pyrites, nor even with merely a metal plate between, but must be separated from it by a brick arch. In other cases there is immediately over the burners a gas-flue, serving at the same time as a dust-chamber, on the top of which the acid-pans are placed (see the diagrams of Malétra's burners, figs. 76, 77). Sometimes, if there is any fear of leakage from the pans into the burners, they are not placed over these, but upon a continuation of the gas-flue.

Hasenclever even advises building a second gas-flue, to be used when the pans have to be repaired. The heat of the kiln-gas will not thus be turned to account so well as if the pans stood directly upon the burners; and the danger of leakage into the burners can be avoided by providing the metal plates, on which the pans rest, with a flange all round and an outflow for any acid collecting in it, like those used in nitre-ovens. But, on the other hand, it has been noticed that sometimes, especially in the case of poorer ores, the pans on the burners withdraw too much heat from these to be conducive to good burning.

Whilst at some places such pans on the top of the burners concentrate all the chamber-acid from 112° to 144° Tw., at others this cannot be done, and a little extra coal is required for completing the concentration.

The diagrams, figs. 237 to 243, represent pans designed by Bode, along with the pyrites-kilns used by him. The apparatus shown here belongs to a set of chambers of 40,000 cubic feet capacity; and each burner receives daily 16 cwt. of Westphalian pyrites containing 42 per cent. of sulphur. The grate of each burner has a surface of 34·4 square feet; the grate-bars are elliptical, 3 inches by 1½ inch, each of them movable; the arch is 4 feet 4 inches above the grate, with a spring of 7 inches. The diagrams show how each burner can be cut off separately. The pans are 6 feet 3 inches by 4 feet

Fig. 237.

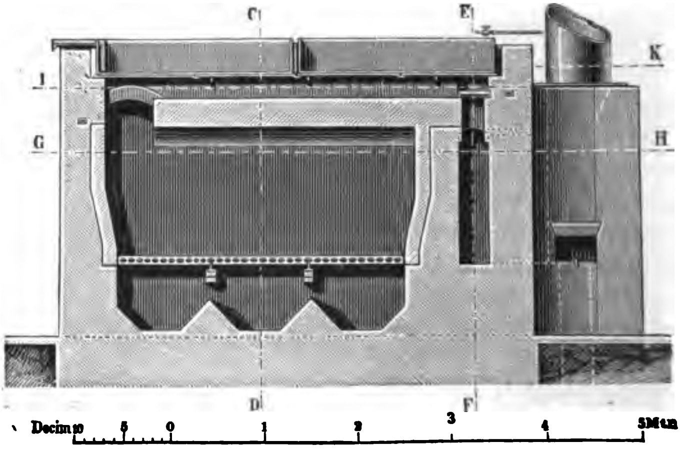


Fig. 238.

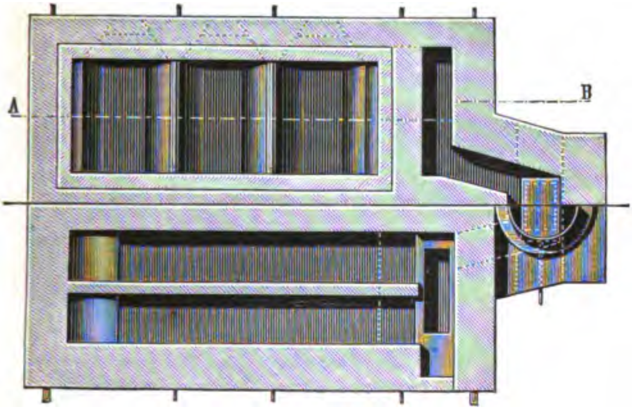
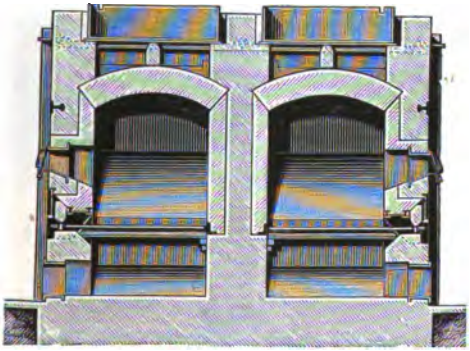


Fig. 239.



2 inches by 1 foot 2 inches, made of sheet lead weighing 8½ lb. per superficial foot. They supply daily, when 1½ ton of pyrites is burnt, altogether 2 tons 5 cwt. of acid of 144° Tw. (that is to say, 5 cwt. in excess of the make of the chambers); but as at the same time from 15 to 18 cwt. daily have to be evaporated for the Gay-Lussac tower, the excess causes no inconvenience. Each year three new pans used to be put in, a pan never being left until actually burnt through, but replaced as soon as the lead had become too thin—a plan most decidedly to be recommended in every case. The renewal

Fig. 240.

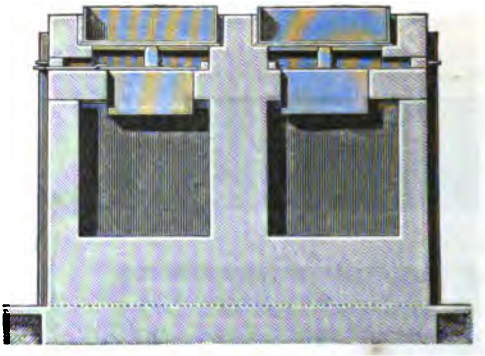


Fig. 241.

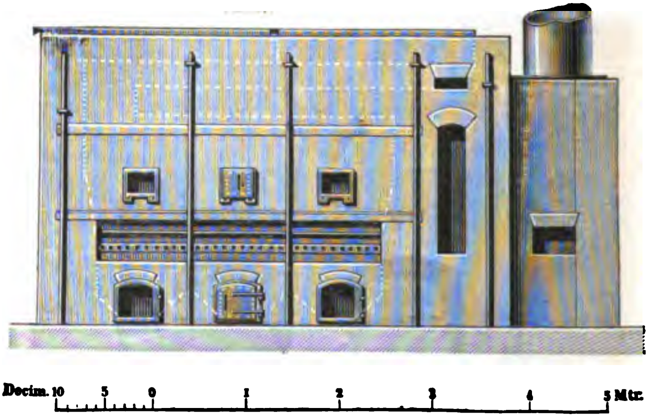


Fig. 242.

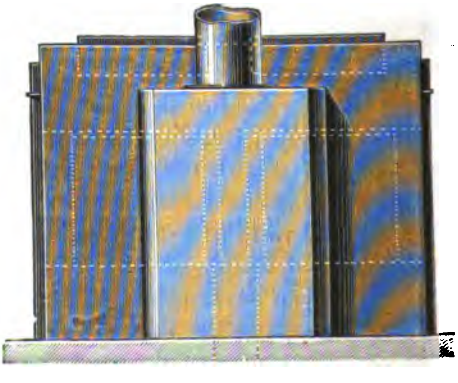
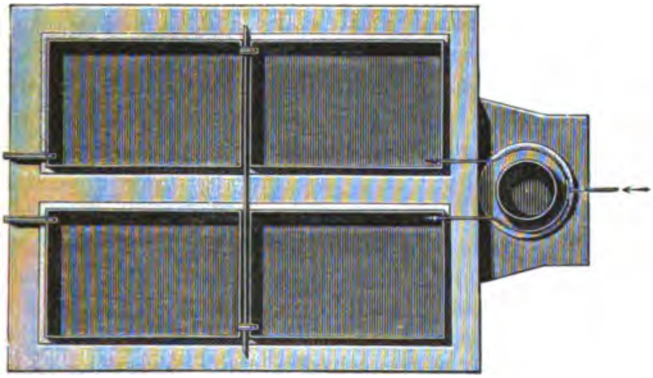


Fig. 243.



only refers to the strong-acid pans; those for weak acid are hardly injured at all. The former are therefore much better made of thicker lead, say 30 lb. to the superficial foot, in which case they last for about two years.

The cost of concentration with such pans only amounts to a small fraction of the wages of the burnermen, in addition to the expense of renewing the pans; Bode calculates it, for a special case, at 4½*d*. per ton of strong acid; for less-favourable cases he estimates it at 6*d*. to 9*d*. per ton.

4. *Concentrating-pans heated by high-pressure steam in lead coils.*

According to Hasenclever (Ber. d. deutsch. Chem. Ges. v. p. 504), the first idea of concentrating sulphuric acid by means of indirect steam we owe to Carlier, the Manager of Messrs. Curtius' chemical works at Duisburg. After several trials at that works they now use wooden tanks lined with lead, 13 feet square, on the bottom of which lie two lead coils, each of 150 feet length, 1¼ inch bore, and ¼ inch thickness of lead, for conveying steam of 45 lb. pressure. The bottom of the pans is shaped like a truncated pyramid, for the purpose of more easily running off the condensed water; so that the tanks are 2 feet deep in the centre, 1 foot deep at the sides. The two ends of each steam-coil are connected with a lower-placed steam-boiler, into which the condensed water continually flows. When the acid has arrived at 140° Tw., it is run into a leaden tank, through which a lead coil runs; the fresh chamber-acid runs through this coil; and, in cooling, the strong acid gets a preliminary heating. With the above apparatus 5 tons of strong acid can be obtained from chamber-acid of 106° Tw. every 24 hours, by the consumption of 9 cwt. of coals. The steam-boiler requires only as much fresh water as gets lost through leakage at the flanges &c. It is advisable to make a wooden hood over the steam-tank, to prevent any danger from acid being splashed about in case of a steam-pipe bursting. Owing to the low temperature, no acid at all is evaporated; the process is very cleanly, and economical as to consumption of fuel and labour. This Report of Hasenclever is fully borne out by Bode. Hasenclever (Hofmann's Report, 1875, i. p. 185) states the corrosion of lead to be equal to 0·44 lb. of lead per ton of acid. The steam-pipes are mostly acted upon in the places where they dip into the acid, because the dust accumulating there raises by capillarity some acid above the level of the remainder, and this becomes too highly concentrated by evaporation. Since a lead jacket has been burnt to the steam-pipe at the place in question, the above drawback is no longer observed.

Figs. 244 and 245 represent a similar apparatus, after Bode's 'Gloverthurm,' p. 27. The tank here measures 10 feet 6 inches by 14 feet 9 inches at the surface, 1 foot 4 inches depth in the centre, 1 foot at the sides, is heated by steam of 37 lb. pressure, and supplies in 24 hours 5 tons of acid of 144° Tw. with a consumption of 10 cwt. of Silesian coal. At some works Bode found a consumption of only 8 cwt., at others, however, from 15 to 18 cwt. of coal for the same quantity of vitriol.

The steam-coil must have a valve both where it enters and where it leaves the pans, which should admit of being closed from a distance in case of the coil bursting. Both the coil and the return-pipe for condensed water must be so laid that the water cannot cause a stoppage anywhere. The lining lead weighs from 6½ to 10 lb. per superficial foot. The whole cost of concentration by these pans, including labour, wear and tear of the pan-lead and of the steam-boiler and coils (using 9 cwt. of coals for 5 tons of vitriol), is calculated by Bode at 1*s*. 8*d*. to 1*s*. 10*d*. per ton of strong acid.

Some manufacturers are afraid of running the condensed water back into the boiler, lest the latter should be damaged by any

Fig. 244.

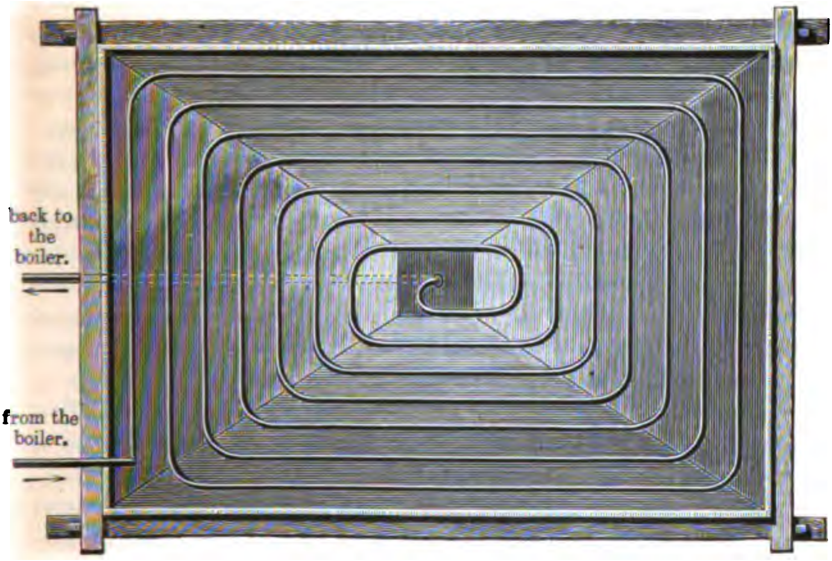
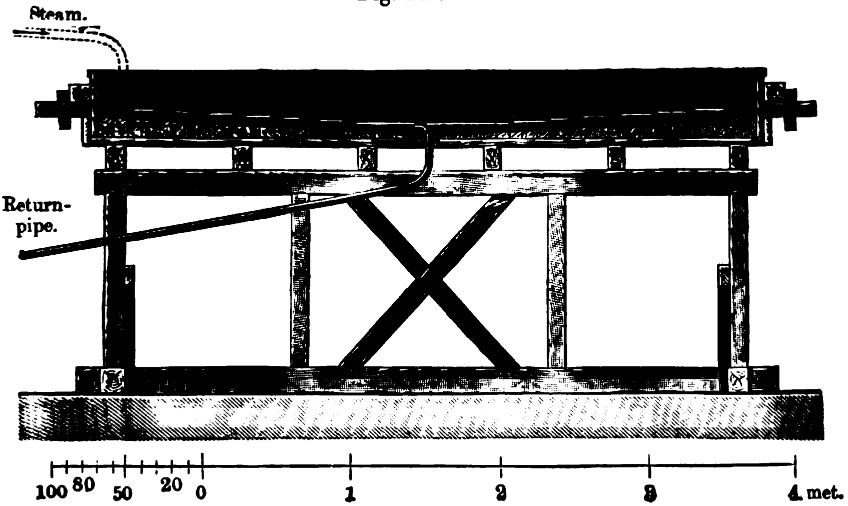


Fig. 245.



acid getting into it, or even caused to explode; in such cases the above-mentioned larger quantity of coals is used. Bode points out that there is no danger of acid getting into the steam-boiler, because in case of the steam-boiler bursting the steam blowing off will prevent the acid from entering the boiler. The return-pipe must not end below the water-line, but in the steam-dome.

The process of concentration by steam certainly furnishes the purest acid, and was considered cheaper than the other plans, excepting the Glover tower or the pans placed on the pyrites-burners. It has been introduced into several German works, but not generally, more especially because there is not everywhere a special steam-boiler handy for it; and some, perhaps, shun it as dangerous. Latterly the reports on the economical working of that plan have not been so favourable as formerly.

Of the other processes for concentrating vitriol up to 144° Tw., none of which has been extensively employed on the large scale, the following may be mentioned here:—

Concentration in platinum dishes, in Faure and Kessler's apparatus. The inventors state that 7 parts of coal suffice for obtaining 100 parts of vitriol of 144° Tw. from vitriol of 106° Tw., of which quantity 4½ to 5 parts of coal may be deducted if the steam be used for the acid-chambers. The same might be done in any other plan; but it rarely is done, because too much air is carried along as well. According to Bode, in reality 10½ parts of coal are used, the warm water being utilized for feeding a boiler. This system, applied to concentration up to 144° Tw., does not seem to be able to compete even with the steam-pans, let alone the burner-pans or the Glover tower, least of all if the cost of plant be considered.

Stoddart (Chem. News, xxiii. p. 167) has proposed to force a current of air into vitriol heated in a pan; acid of 140° Tw. is stated to be obtainable in this way if the temperature be 150° C., and the strongest oil of vitriol at a temperature of 260° C. This plan, if ever carried out on a large scale, was no doubt very soon given up again. There is no reason why a current of air should not do much more harm by cooling the acid than it can do good by carrying away the vapour more quickly, the latter being done much better by top fire, where there is also no danger of splashing. It is well known that lead pans would not very long stand a temperature of 260° C.

Galletly (Chem. News, xxiv. p. 106), who had applied the same principle independently of Stoddart, only worked with a small lead box, 18 inches by 12 inches, in which he obtained from brown vitriol (sp. gr. 1·745) 5 gallons of vitriol of sp. gr. 1·83 by keeping the temperature at 205° C. for one hour, and forcing 16¼ cubic feet (roughly measured) of air through the liquid. There was a loss of 11·19 per cent. of acid in this process, as against 8·8 per cent. when using glass retorts. He believes this acid to be recoverable by passing the air into the chambers, forgetting the harm which such a large quantity of air would do there. He states very candidly that a Glasgow manufacturer tried his plan without getting it to succeed; but (very naturally) he retains his belief in the efficacy of his plan all the same.

Seckendorff (Wagner's Jahresb. 1855, p. 56) proposed to concentrate the vitriol in flat-bottomed iron retorts completely surrounded by fire. The retorts are to be filled with lead sulphate, sand, or gypsum; chamber-acid is to be run in till a paste is formed; and the retorts are then to be heated. The watery vapour first appearing is conducted into the chambers; the concentrated vitriol coming after this is to be collected in glass or stoneware vessels, and is said to be very pure, free from iron, and as concentrated as that from platinum; nor is the iron retort said to be acted upon very strongly. Probably this plan has never been actually tried at all.

The concentrating-method of De Hemptinne forms a part of a peculiar complete arrangement for manufacturing sulphuric acid, which will now be described connectedly, from the report and the comments of Bode (Dingler's Journ. ccxvii. p. 300). The author's own criticisms will, as usual, be put within brackets, [ ]. The chemical process in this case is identical with the general one; the principal point is the diminution of chamber-space, on the same lines as Verstraet and Ward (see pp. 283, 284) had previously but unsuccessfully attempted it.

Figs. 246 and 247 represent the apparatus proposed by Hemptinne. The sulphurous acid is generated in the furnaces A by burning pyrites. The burners are arranged in a circle, in order to save brickwork, to lessen the radiation of heat, and to cause equal draught for every compartment. The spaces B are covered with metal plates, and serve as dust-chambers. The gas ascends in the brick stack D, travels through the large horizontal flue C, and enters the first lead chamber F. The cover of the flue C is

Fig. 246.

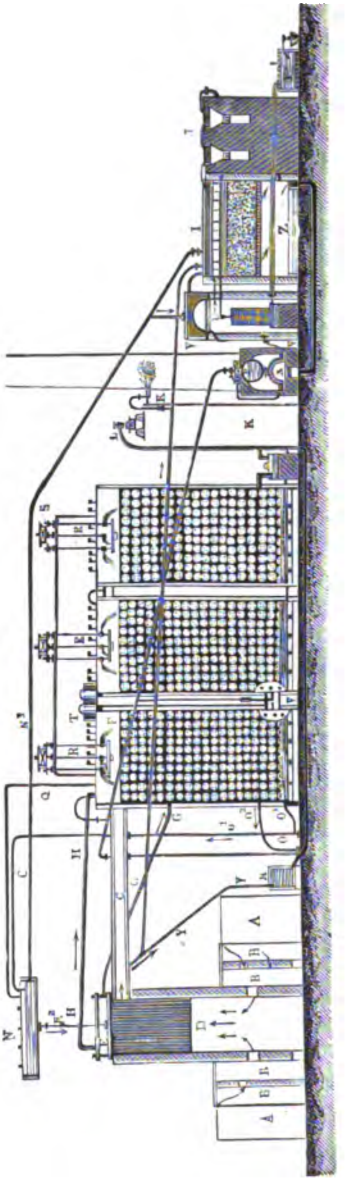


Fig. 247.

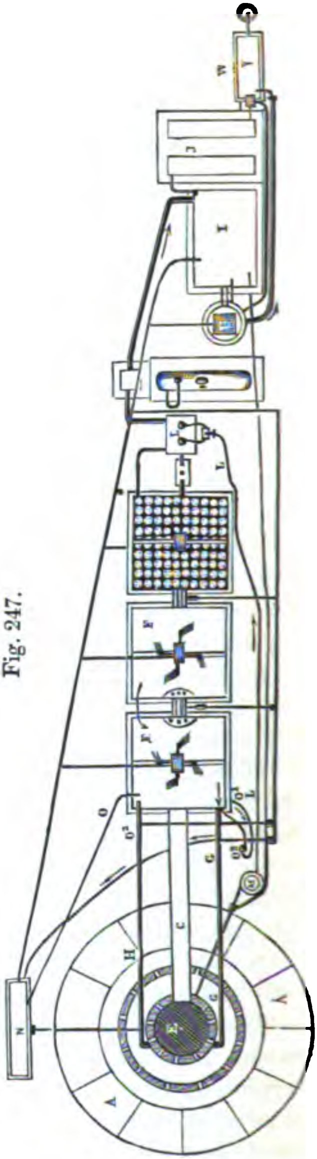
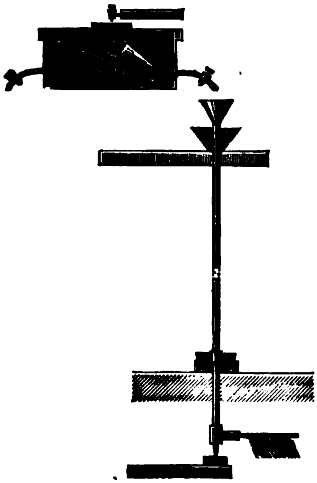


Fig. 248.



formed of corrugated sheet lead, and can be cooled by water. The heat of the burners is utilized for concentrating vitriol—but indirectly, as the direct use of it in the Glover tower is said by Hemptinne [who evidently has had no practical experience of it] to have certain drawbacks. For this purpose the brick stack D is covered with a leaded metal plate carrying a lead pan E, from the bottom of which 100 lead tubes of 3 feet 3 inches length and 4 inches bore hang loosely down within the stack; they are closed below, but open at the top, and burnt to the bottom of the pan. Each of them contains a narrower lead tube (similar to the tubes in Field's steam-boilers), whose open lower end supplies cooler acid at a distance of 4 inches from the bottom of the wider pipe. The energetic movement of the liquid is supposed to prevent the deposition of impurities within the pipes. The whole set of pipes has a heating-surface of about 1300 square feet. In order to facilitate the circulation of acid, the narrow tubes are burnt to a special sheet of lead with turned-up edges, resting on acid-proof bricks, with which the bottom of the pan E is covered. Fig. 248 shows this more plainly. Evidently there may easily be rents at the innumerable joints, which, as Hemptinne says, do not matter, because the tube in question can be dispensed with by plugging up the opening. But Bode justly points out that in the hot acid no plugs but badly-fitting ones of lead or stoneware can be used, that it will be very difficult to find out any leaks, and even more difficult to fix the plugs, especially if, according to Hemptinne's proposal, the pan E be covered for the purpose of denitrating the Gay-Lussac acid. This is to be done by aspirating sulphurous acid into E from the first lead chamber, F, through G; H takes the gas back into the chamber; and a steam-jet at its entrance causes the aspiration of sulphurous acid to the pan and its return along with the expelled nitre-gas. The sulphurous acid is preferably taken from the chamber, in order to avoid flue-dust. [Most certainly mere superficial contact with sulphurous acid will *not* denitrate the Gay-Lussac acid any thing like sufficiently.]

The chamber-acid, mixed with the nitrous vitriol of the Gay-Lussac tower K, is forced through the injector O and the tube O^1 into the vessel N; the feeding of E takes place continuously by the tube N^2, furnished with a stopcock, its contents running off by the overflow-pipe L. The worm M serves for cooling the acid, which again serves for the Gay-Lussac tower. In case of need the concentration is further advanced in the pans I and J; it cannot be carried in the tube-apparatus beyond 148°. [This will be easily believed, since even a plain pan suffers far too much at that strength, let alone one with 100 joints!] The acid is therefore forced upwards only once, against twice for a Glover tower [but nothing like so high in the latter one!].

The lead chambers F, which "quickly" convert the sulphurous acid into sulphuric acid, are of sheet lead one fifth of an inch thick [that is, nearly twice the thickness of that of the usual chambers] and filled with 5200 jars of acid-proof ware, provided with round holes of ¾ inch diameter. The nitric acid is supplied from a glass vessel T by a cock and a Welter's funnel. The vessel T is connected with several similar ones by glass siphons. The 5200 jars stand on a pavement of acid-proof bricks, to avoid damaging the lead, and present a condensing-surface of 84,000 superficial feet. [These jars will form a structure of very little stability, and will certainly not only press upon the chamber-bottom, but very heavily against the sides, which must give way directly whenever the jars loose their hold.]

From the vessel N and the pipe N^3 sulphuric acid is continually run in and spread periodically over the jars by the oscillating troughs S and the glass reaction-wheels R. Excepting the steam-jet K^1 between the Gay-Lussac tower and the chimney, Hemptinne asserts, no other steam-jets are applied, because they partly destroy the nitre-gas—forgetting that he had expressly indicated a steam-jet in the pipe H, and drawn two others between the first and second, and between the second and third chambers! And in H the nitre-gas is exposed to the "destructive" action of the steam much more than in the chambers! [The inventor starts from the view, long exploded, that the formation of vitriol in the chambers is a process of "condensation," analogous to the distillation of liquids, requiring a large surface, and that the principal action of the chamber-steam consists in forming "condensing-molecules," which are much better replaced by the jars, each of which is a "working cell" for producing vitriol! Practice has long since proved that the acid-forming reactions take place in the homogeneous mixture of gases contained in lead chambers, without the intervention of surfaces.]

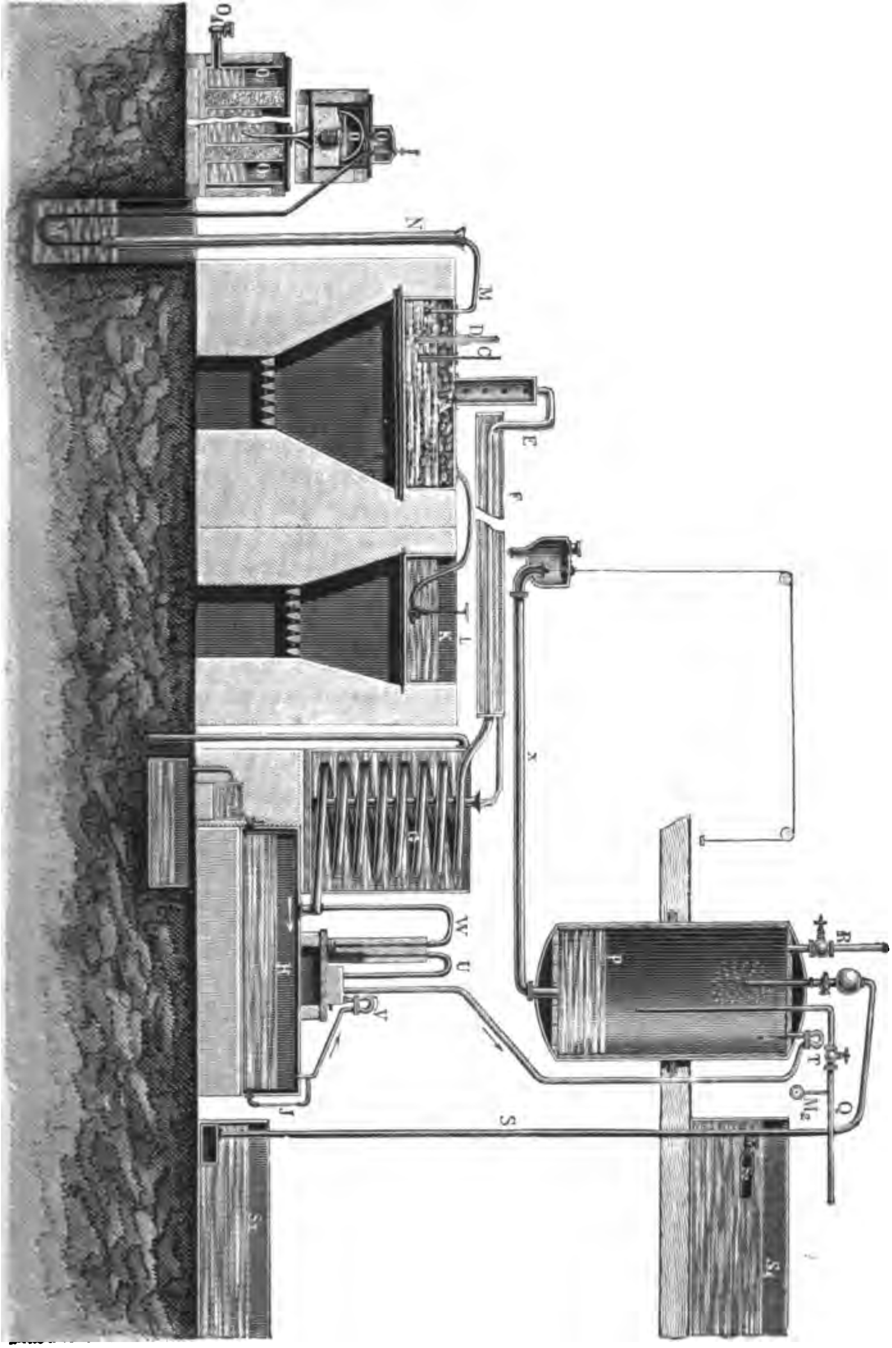
The acid taken from the bottom of the first chamber by the pipe O^2 is forced by the injector O into the vessel N. The injector consists of an alloy of lead with a platinum nozzle of such bore that the chamber-acid is diluted to a suitable degree. The steam condensed in the injector thus takes the place of the ordinary direct chamber-steam. A side branch O^3, ending in the chamber, aspirates SO_2 from it, the denitration thus beginning already in the delivery-pipe O^1. This mixture thus gets into the vessel N, which is covered and lined inside with acid-proof bricks, basalt, or glass. The gas passes back into the chamber by Q. N^1 is a glass float within a bell jar, indicating the level of acid in N.

The concentration of the vitriol up to 170° Tw. is to be effected by superheated steam introduced into the tower U after having passed a box U^1 filled with asbestos. The tower is cylindrical, made of hard-burnt bricks ("clinkers"), and contains a stack of 504 small boxes of pottery, over which the acid trickles down. The cover of the tower is formed by a cylindrical lead pan V with arched bottom, cooled by acid from N; the acid runs over into the pan I. Below this lead pan a gutter collects the condensed weak acid and carries it away through the overflow V^1 to the outside. The hollow little boxes forming the stack are made of acid-proof English stoneware, 6 inches square, with six holes of 2½ inches diameter; they must form perfect cubes to make the stack stable. The acid coming from the pans I and J by the oscillating trough W, being first filtered, is divided into a spray either by a small reaction-wheel or a platinum rose, and runs over the pottery-boxes. The superheated steam is generated in the cast-iron vessel X filled with scrap copper and heated by the fire of the steam-boiler P or separately. At the bottom of the stack the concentrated acid collects in a lead pan with double walls, the space between which is filled with iron balls, water continually circulating between them and cooling the pan. The concentrated acid is taken to a collecting-tank Y by a lead pipe surrounded by a copper jacket and cooled by water. The steam left behind in U passes under the lead pan I, and causes here the concentration of the acid up to 144° Tw. The acid vapours not yet precipitated at the bottom of V pass through a layer of scrap iron heaped up on a grate and from time to time sprinkled with water; the resulting copperas-liquor collects in the pan Z; the remaining vapours and gases pass through an underground flue into a chimney.

Hemptinne claims the following points as his improvements in acid-making:—(1) Concentration in Field's tubes by the waste heat of the pyrites-burners, along with denitrating the chamber-acid and the nitrous vitriol without contaminating it by flue-dust. Bode shows that Hemptinne has misunderstood Field's principle, that there will be little circulation of acid, and hardly efficient denitration. [We may safely call the apparatus utterly inefficient for denitration and of impossible construction for practical work.] (2) "The first practical employment of the principle that the formation of sulphuric acid is much more a question of surface than of space." His chambers with jars of 84,000 superficial feet are said to cost 26,000 francs, whilst the same surface of 7 lb. lead, which is used up after twelve years, costs about 175,000 francs. It has been mentioned above, and has been proved again and again, that the "principle of condensation," which is any thing but new, is altogether wrong; and the chamber-lead is certainly in great part recovered at the end of the twelve years. (3) "Doing away with steam." It has been shown how strikingly Hemptinne contradicts himself in that matter. (4) "Quicker work" falls to the ground with point 2. (5) "Employment of an injector for pumping, heating, and denitrating vitriol." [How long will such an injector last ?] (6) "Concentration by superheated steam"—but in an almost inaccessible apparatus, easily damaged, probably with greater cost than by direct firing, and causing a stoppage of the chambers when it has to be repaired.

Thus De Hemptinne's process, in spite of being patented in several countries, does not bear the stamp of practical applicability.

Fig. 249.



Another concentrating-system of De Hemptinne's, published by him in 1872 (Dingler's Journ. ccv. p. 419), cannot, like the method just described, at once be called impracticable; but, for all that, it has not, in the long run, been a success. It starts from Kuhlmann's results of experiments made in 1844, according to which (1) sulphuric acid of 170° Tw. at a mercurial pressure of only 1¼ to 1½ inch boils already at 190° to 195° C., and (2) sulphuric acid does not sensibly [?] act on lead at temperatures not exceeding 200° to 205°. [Kuhlmann's results have been refuted by those of Hasenclever and Bauer, p. 41, both proving that lead is acted upon far below 200° C.] Hemptinne therefore endeavoured to avoid the last concentration of vitriol in costly platinum or fragile glass by employing a vacuum—a plan already proposed in a much less complicated form by Keller thirteen years previously (Wagner's Jahresb. 1859, p. 139). The concentration of the vitriol up to 170° Tw. takes place in the small vacuum-boiler A (fig. 249) made of lead, filled with boulders or balls made of pottery or glass of 1¼ to 1½ inch diameter, in order to resist the inward pressure of the atmosphere. The partial vacuum is produced by the condensation of steam in an iron boiler, lined with wooden staves inside so as to avoid unnecessary heating of the iron. The steam, entering through Q, soon drives out the air through R. A spray of water injected by S at once causes a vacuum of 27½ to 28 inches, as shown by the barometer U. The first condensation is effected by the water in the copper ball S, the second one by water from the tank S_4, aspirated from the filter S_2; the last condensation is caused by the water aspirated from a tank S_3 or a moderately deep well and filtered. When the vacuum is as nearly perfect as possible, the cock V is opened and the air is removed from all parts of the apparatus. Now the fire is lighted under the pan, the acid vapours escape through the two domes B and the pipe E lying in a small cooler, and they condense in the worm G; the water of condensation collects in H. The concentration of the acid is known to be finished when the two thermometers C, fixed at opposite ends of the apparatus, show 200° to 205° C., and when the small float B no longer exhibits a "dancing" movement. Now the cock Z is opened; air enters the apparatus; and the strong acid is withdrawn, within 4 inches of the bottom of the pan, by a siphon M, dipping into the well of 20 feet depth, and thus forming a barometrical lute. Already before this the fire has been drawn out; and during the drawing-off of the acid a fine spray of water is squirted into the fire-place, to prevent overheating the lead. The hot acid is first cooled in the apparatus N and then in O, and is then passed through the filter O_3, consisting of perforated lead cylinders filled with asbestos, quartz, sand, or pounded glass, in order to retain the lead sulphate which it holds in suspension. Or large settling-tanks may be used, in which the acid, protected from the air, becomes clear in three or four days. In the meantime the apparatus has been emptied again, and has been refilled with acid from the tank L by means of the stoneware pipe and tap K. The tank L serves for a preliminary heating by means of six lead heating-pipes of 5-inch bore, which are not shown in the diagram.

Hemptinne has also made a calculation of the saving in the cost of concentration effected by his plan, which he estimates at 44 per cent. To be sure in this case the erroneous assumptions, which so often make inventors' calculations worthless, are unusually gross, and cannot deceive any body who knows any thing about the matter. The calculation refers to the annual concentration of 20,000 carboys of 2 cwt. each, =2000 tons.

a. *Concentration in platinum.*

	frs.
Loss of platinum 4 kgr. at 900 frs.	3600
5 per cent. interest of 90,000 frs. for platinum (!)...	4500
Repairs	500
440 tons of coal at 20 frs.	8800
	17400

b. *Concentration in a vacuum.*

	frs.
5 per cent. interest on 5 apparatus, costing 3500 frs. each (only !) =17,500 frs.	875
Wear and tear and repairs	3000
280 tons of coal at 20 frs.	5600
	9475

But it is not explained why the enormously exaggerated sum of 90,000 frs. (=£3600) is assumed for a platinum apparatus at 2000 tons annual output, and the ridiculously small sum of 3500 frs. (=£140) for one of his complicated apparatus, nor why so much more coal should be used for boiling down in a thin platinum boiler, than in a thick lead boiler, together with those required for producing the vacuum &c.

The best proof that Hemptinne's apparatus has not been very successful is, that he describes a new one ('Bulletin du Musée de l'Industrie de Belgique,' Sept. 1877, p. 121; abstracted by Bode, with a diagram, in 'Dingler's Journal,' ccxxvii. p. 74), in which he returns to platinum, viz. an open pan with a cover made of pipes and plates of toughened glass, filled with asbestos, platinum wires, air-courses, &c. In regard to it we must refer the reader to the original.

The last Concentration of Sulphuric Acid.

We have seen that we cannot carry on the concentration in lead pans beyond 144° or, at the outside, 152° Tw., the latter not without a somewhat strong action upon the lead. In the Glover tower it is possible to go rather further, as its lead is protected by the lining so as to be acted upon very slightly: the acid does not come into contact with the lead, but only with the flints, bits of pottery, coke, &c., and arrives at the bottom with a temperature of about 130° C.; so that even the bottom of the tower, which is made very strong, is not sensibly acted upon. In fact those manufacturers (being the majority) who work the Glover tower with hot gas from rich ores, and get their chamber-acid up to 120°–124° Tw., regularly attain a concentration of 152° Tw.; and in some cases even 156° or 160° is reached. The latter is the exception, and perhaps already somewhat dangerous to the tower; if, however, it is not so, this concentration by hot kiln-gas in the Glover tower (probably modified to some extent) seems to be the cheapest and safest plan for the last concentration of the vitriol, because in it the escaping gas goes into the chambers and is not lost at all.

Concentration beyond the point attainable in lead pans or in the Glover tower is a much more difficult task, involving incomparably more expense than the first concentration. Since the attempts to concentrate the vitriol up to 170° Tw. by means of cooled lead pans with top-heat (Clough), or by a vacuum (Keller, De Hemptinne), or in iron retorts (Seckendorff), or in towers filled with pebbles and heated directly by heating-gas (Gossage), and others have not been successful, recourse must still be had to apparatus made of glass or platinum, of which the former have the drawback of very restricted size and great liability to breaking, the latter that of being very costly without being proportionately durable. The circumstances make their application both expensive and troublesome.

By far the largest quantity of vitriol is used of certainly no higher strength than is attainable in lead, mostly even rather weaker. For making sulphate of soda—that is, ultimately soda ash—the acid is never taken stronger than 144° Tw., generally only 140° Tw. The English manufacturers as a rule dilute their Glover-tower acid down to this point with chamber-acid; or they only make as much acid of 152° in the Glover tower as is required for working it, and they keep the remaining acid weaker by running more chamber-acid through it. For superphosphate the acid is mostly employed even in a weaker state; and this, along with the sulphate of soda, swallows up most of the total quantity of vitriol made. In the great majority of cases, to be sure, sulphate-of-soda and superphosphate works make their own sulphuric acid, and, of course, do not concentrate it beyond their own requirements.

Touching the acid made for sale, however, a circumstance has to be considered here which in many cases induces the manufacturer to incur the great expense and trouble of concentrating the vitriol as highly as possible, even in cases where the consumer, not requiring it of such strength, must himself dilute before using it. This is the greater expense of package and transit for the same weight of real acid in the dilute as compared with the concentrated state. Apart from those cases in which completely concentrated vitriol is asked for on account of the smaller cost of package and of transit, or from old habit and ignorance, there are many cases in which the consumer is really obliged to employ an acid of the highest possible strength:—for instance, the purification of rape-oil; that of benzole, paraffin, and other mineral oils; the refining of gold and silver; the production of nitro-cellulose, nitro-glycerine, nitro-benzene, and other nitro-compounds; that of the sulpho-acids of benzene and anthraquinone for the manufacture of resorcine and alizarine; for dissolving indigo, and many other purposes. In many cases an acid containing from 93 to 94 per cent. of SO_4H_2 will do; and often that which is sold as acid of 170° Tw. does not contain any more, and really ought to show only 166° Tw. ($=1{\cdot}83$ sp. gr.). For making nitro-compounds especially, however, an acid of greater strength is required, containing 97 or 98 per cent. of SO_4H_2; and this cannot show more than 1·840 sp. gr. at 0°, or 168° by a really true hydrometer; but the ordinary Twaddle's hydrometers mark the point of 1·83 specific gravity by 170°, instead of 166°. We shall see below how the stronger acid just mentioned can be obtained. Sometimes an "extra-concentrated" acid is asked for, equal to that obtained by distillation, and possessing 1·842 specific gravity. Even this is not the pure hydrate, SO_4H_2, but contains 1½ or 1½ per cent. of water. It is better not made directly on the large scale, because the apparatus would suffer too much (see below), but by mixing ordinary strong acid with a little fuming (Nordhausen) oil of vitriol. Certainly such acid of 99½ to 99¾ per cent. SO_4H_2 has been made on a very large scale in platinum boilers (see below) by Scheurer-Kestner. These strongest acids are mostly required for dissolving indigo, and for making the organic sulpho-acids.

It has already been mentioned that either *glass* or *platinum* vessels are used for the last concentration of sulphuric acid. Which of these two materials is to be preferred to the other has been a matter in dispute for a long time; nor is it settled now, both systems being largely employed. Formerly, before the platinum industry was developed, *glass retorts* were the only available apparatus, and those could only be had of comparatively small size and bad quality. They were also mostly set in "galley furnaces," a double long row of retorts being heated by a fireplace at one end; thus the retorts near the fire were, of course, much more heated than the distant ones, and were much sooner finished, or even overheated before the distant retorts had been sufficiently fired. Each retort was either put into a metal pot, with some sand between, or protected from the direct flame by a covering of clay and horse-dung. Both owing to the inferior quality of the retorts and the unsuitable setting, there was always much breakage, combined not only with the loss of acid, but also with the sudden evolution of suffocating vapours. The cracking of the retorts was especially induced by a cold draught getting at them; and since in that case the workmen had to save themselves instantly from the vapours by leaving the room, frequently the cracking extended to all the retorts. Besides, the expenditure of time, wages, and fuel in this process was very great.

There was always, therefore, an inducement to discover some other material than glass; and the only practicable metal, *platinum*, was at once applied, in spite of its high price and difficult management, as soon as Wollaston's process of welding spongy platinum into ingots and plates was made known. The first still appears to have been made in 1809 at London; it weighed 423 ounces ('Chem. News,' xxxviii. p. 43). At that time platinum stills, weighing from 66 lb. to a cwt., were made, holding 4 to 6 tons of vitriol, and costing from 40,000 to 50,000 frs. (£1600 to £2000). This large sum did not deter manufacturers from using platinum for the last concentration of vitriol, because they convinced themselves at once of the large amount, facility, and safety of the work of concentration that could be carried on in them, and because they thought they could reckon upon such apparatus lasting almost for ever.

The platinum vessels made by Wollaston's process were, to be sure, often porous and unsound, so that vitriol oozed through; besides, blisters and rents frequently appeared in them, which had to be soldered up with gold. The platinum stills themselves, therefore, gave much dissatisfaction. This, however, has been much diminished since Ste.-Claire Deville taught the melting of platinum in large masses by an oxygen-gas blowpipe in furnaces made of quicklime, casting perfectly sound ingots of it weighing 2 cwt., and, further, to solder the joints with platinum itself instead of gold, analogous to the burning of the lead chambers. In London this process was first applied in 1860. Since then the stills have been much more durable and at the same time cheaper, although the monopoly of the raw material by the Russian Government, and the unavoidable concentration of the platinum-industry in very few hands, still tend to keep the price of platinum apparatus at a very high figure.

When, however, attention was drawn to the fact that platinum itself is gradually acted upon by sulphuric acid (see below), and that thus the large capital expended on the stills not only involved heavy permanent charges for interest, but would have to be gradually written off altogether, and when, on the other hand, great improvements were effected in the manufacture and treatment of glass retorts, the latter came to the fore again, and began to drive platinum vessels out of the field, more especially in England. In 1862 Hofmann mentioned, in the 'Report of the Jury,' that in Lancashire the use of platinum retorts had almost ceased; at that time about $\frac{7}{10}$ of all the vitriol in England was concentrated in glass. In France and Belgium glass retorts existed along with platinum; but the latter held a wider ground; and in Germany it was almost exclusively used. In 1868, the 'Official Report of the International Jury,' vii. p. 34, states that concentration in glass was then very rare (in France).

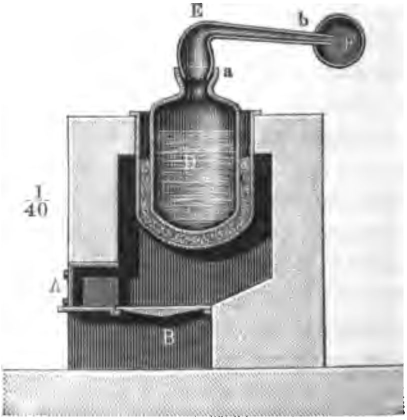
In order to meet the competition of glass, the platinum-works made efforts to construct the stills more durable and more cheaply; and they have indeed recovered a portion of the field previously lost. Very recently they have been urged on to renewed efforts in this line by the combination of platinum and lead employed by Faure and Kessler.

At this moment the matter stands thus:—Both glass retorts and platinum stills are in use, some of the latter made according to the old and others according to the new system. The glass retorts are mostly used for the rather less concentrated acid, containing 91 to 92 per cent., the platinum stills for the more concentrated acid, 93 to 94 per cent.; in a few cases both are employed at the same works for these different objects. The glass retorts, however, are almost entirely confined to England, and in Lancashire are almost exclusively used; on the Continent, platinum vessels are used nearly everywhere but in a few places exceptionally well situated for obtaining glass retorts—for instance, Montpellier, where, according to Payen, a retort of 18 gallons capacity only costs 1·6 franc, whilst at Paris and most other industrial centres the price is 6 francs. Since such a retort holds a little over 1½ cwt. of strong vitriol, and on an average can be used five times, furnishing altogether 8 cwt. of vitriol, the retorts for 1 ton of acid at Montpellier cost 6 francs, at Paris &c. 15 francs.

Concentration in Glass Retorts.

The former shape and setting of these have been mentioned above; here we only treat of the kind now in use, which has almost entirely superseded the older. We will only remark that the old retorts could hardly be made larger than so as to furnish 1½ cwt. at each operation, and that they were made from glass poor in alkali, which is less acted upon by vitriol than that rich in alkali. The weak acid distilling during the operation is collected in carboys, into which the necks of the retorts project. As soon as the acid blackens wood when dropped on it, the concentration is considered

Fig. 250.



complete, the furnace is allowed to cool down, and the acid poured into the storage-vessels.

The shape of glass vessels now in use was introduced by Chance Brothers, of Oldbury, near Birmingham, who make them at their glass-works at Smethwick; it is represented in fig. 250. A is a small fire-door, B the grate, C a metal pot serving as a sand-bath, D the retort itself, entirely surrounded by sand up to the level reached by the acid at the end of the operation, and not merely resting on sand at the bottom, as shown in some diagrams. The retort consists of two separate parts, viz. the bottle-shaped part D, which ends at the top in the neck *a*, and the head E. The latter looks exactly like an ordinary small laboratory-retort with its bottom cut off; it is loosely put into the neck *a*; and its other end, at *b*, enters an aperture in the wide lead pipe F, which runs all along the retort-house. The retorts (in number from 20 to 50) are placed in a separate house, the temperature of which is kept constantly at from 25° to 30° C., it being provided with tight-fitting windows and double doors; only one door opened at a time, the other being shut, so that no draught (the chief cause of the bottles cracking) can enter.

In the pipe F, which conveys the condensed acid to a collecting-tank, there is always a little suction, caused by the chimney &c.; the joints at *a* and *b* therefore need not be luted by any cement; for no vapours can get out, only air being able to enter. Thus the head E can be simply put on and taken off without the trouble and mess of a cement.

The author has seen retorts at work which had a pretty long crack in the upper part of the neck; such cracks must certainly not reach down to the level of the acid in the bottle. The pot C, which some books recommend to do away with, is mostly used in practice; it has the important advantage of preventing the acid from running into the fire when a bottle breaks. In England, "4 (or even 8) retorts" are never "heated by one furnace," as described in the 'Belgian Official Report' of 1854; each retort has its own small fireplace. They are, for instance, about 2 feet 9 inches in height, 1 foot 6 inches in diameter, and have a capacity of 30 gallons; at each operation they furnish from 3 cwt. 14 lb. to 3 cwt. 2 qrs. of concentrated oil of vitriol.

In a specially observed instance, each distillation lasted 12 hours, followed by 12 hours' cooling at night; the acid is then drawn off by siphons of platinum or thin lead tubing with a very narrow orifice, after lifting off the head E. The siphon is filled with cold acid, the narrow opening closed with the finger; the siphon is then put in quickly and the finger at once washed with water. Sometimes all along the retorts a lead pipe is laid down, with openings for each of them, into which the acid runs from the siphons; sometimes the acid is run direct into the carboys, but better first into a lead cooler. Another lead pipe is laid above the retorts, to fill them with acid of 144° Tw.; the acid must run in hot, almost of the same temperature as that still possessed by the retorts; at all events a small portion of acid is left behind in the retort on drawing off, so that it cannot very well crack in filling. Sometimes a tank for holding the warm acid is placed at a higher level than the retorts; from this a long, thin, lead pipe is led first below the bottom of the retorts and then upwards again, being held in its place by a frame. Thus, ordinarily, no acid runs out; but by bending down the lead tube each retort can be filled in turn without using any tap.

Roscoe and Schorlemmer (' Lehrbuch der Chemie,' i. p. 279) give the following diagrams of a kind of retort slightly deviating in shape, and more so in the setting, from that just described (figs. 251 to 253).

Fig. 251.

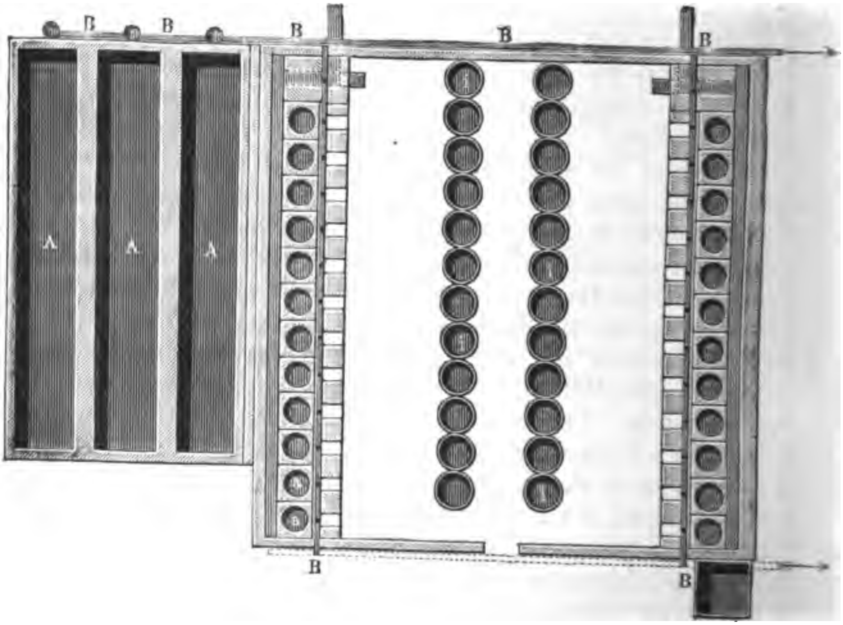


Fig. 252.

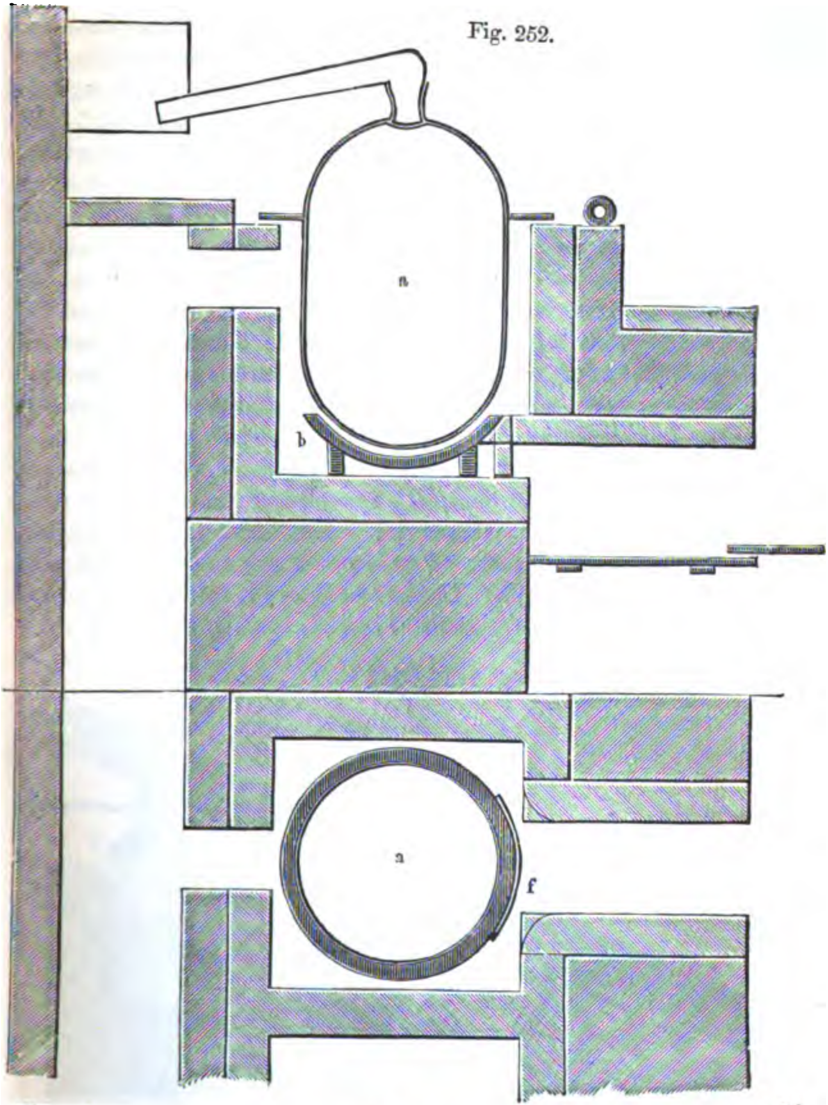
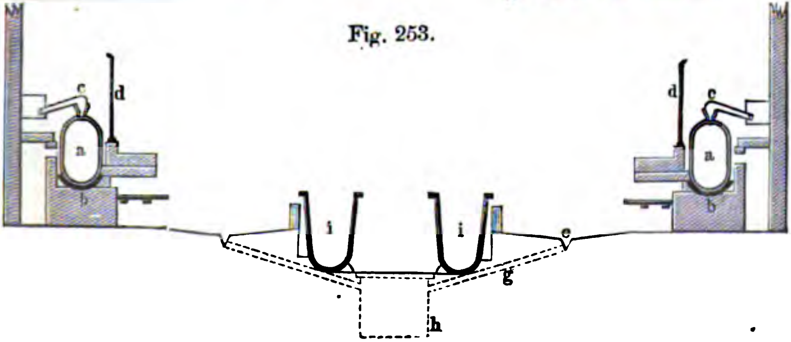


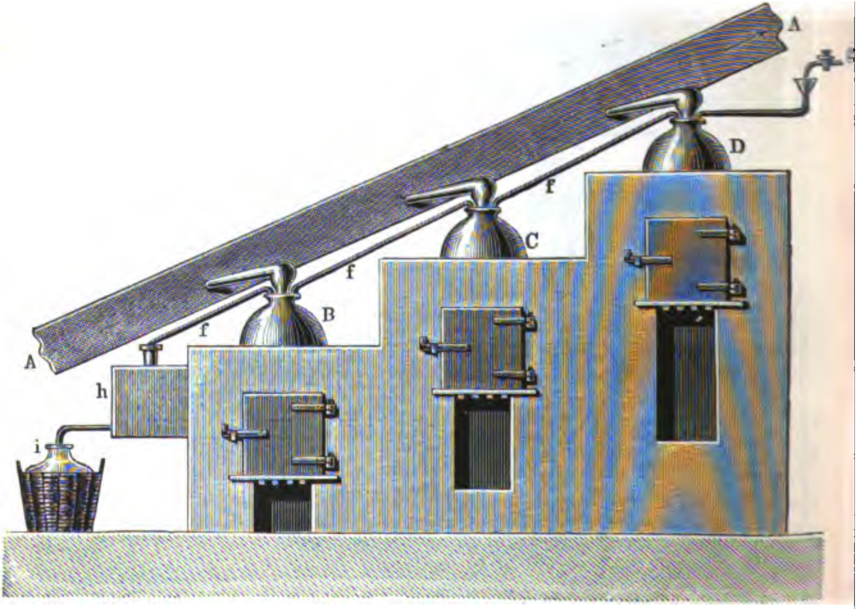
Fig. 253.



A A are boiling-down pans, B B pipes for taking away the acid, *d d* the ascending pipe which is afterwards bent down for filling the retorts (as above). The three pans are sufficient for supplying two "rectifying-houses," each having 24 retorts and making daily 5 tons of acid of 1·84. The concentrated acid cools during the night. It is drawn off by siphons into the cooling-pots *i i*, and filled from them into carboys. The warm retorts are at once filled up again with acid of 144° Tw. Whenever a retort breaks, the acid runs on the inclined floor into the gutter *e*, and thence through the lead tube *g* into the cistern *h*. The retorts are blown of thin glass, as evenly as possible, 3 feet 3 inches high, and 1 foot 10 inches in diameter. They rest on a flat metal sand-bath *b*, and are protected from direct contact with the flame by the round fire-clay slab *f*. The glass head *c* is put on loosely.

According to a patent of Gridley's (1871), several retorts are placed terrace-wise in an obliquely ascending furnace, and are connected by siphons; so that the top retort is fed by fresh vitriol, which, after being concentrated to some extent, flows into the next lower retort, and so forth. The lowest retort is in the hottest part of the furnace. This arrangement, which is carried out at some

Fig. 254.



works, is represented in fig. 254, according to Roscoe and Schorlemmer's 'Lehrbuch,' p. 281. As soon as the acid in B has attained the concentration 1·84, the retorts are connected by the siphons *fff*, and acid of 144° Tw. is run in through the tap *g*, at a temperature of 150° C.; when it has arrived at B, it possesses the necessary concentration, and runs off through the cooler *h* into the carboys *i*. Thus the concentration in glass retorts is rendered a continuous operation, and at the same time much fuel is saved.

In order to prevent the cracking of the retorts by sudden draughts, Jones patented, in 1845, so-called "protectors," consisting of hoods of sheet iron or stoneware, made in two parts, quite covering the neck of the retort. But as this also prevents observation of the liquid, they are inconvenient; and they are quite unnecessary if the house is arranged as described above—that is to say, if it is kept warm, and draughts are excluded by double doors.

As to the cost of concentrating in glass, the labour is, of course, greater than in platinum stills, and it is also of a disagreeable kind. The consumption of fuel is sometimes absurdly stated to amount to eight times the consumption with platinum stills; in direct contrast is the following statement by P. W. Hofmann, referring to the cost of concentration at Dienze, where 2½ tons of vitriol are daily made in glass retorts, viz. for 1 ton:—

	s.	*d.*
4 cwt. of coals	4	0
Wages	3	0
Breakage of carboys	1	0
	8	0

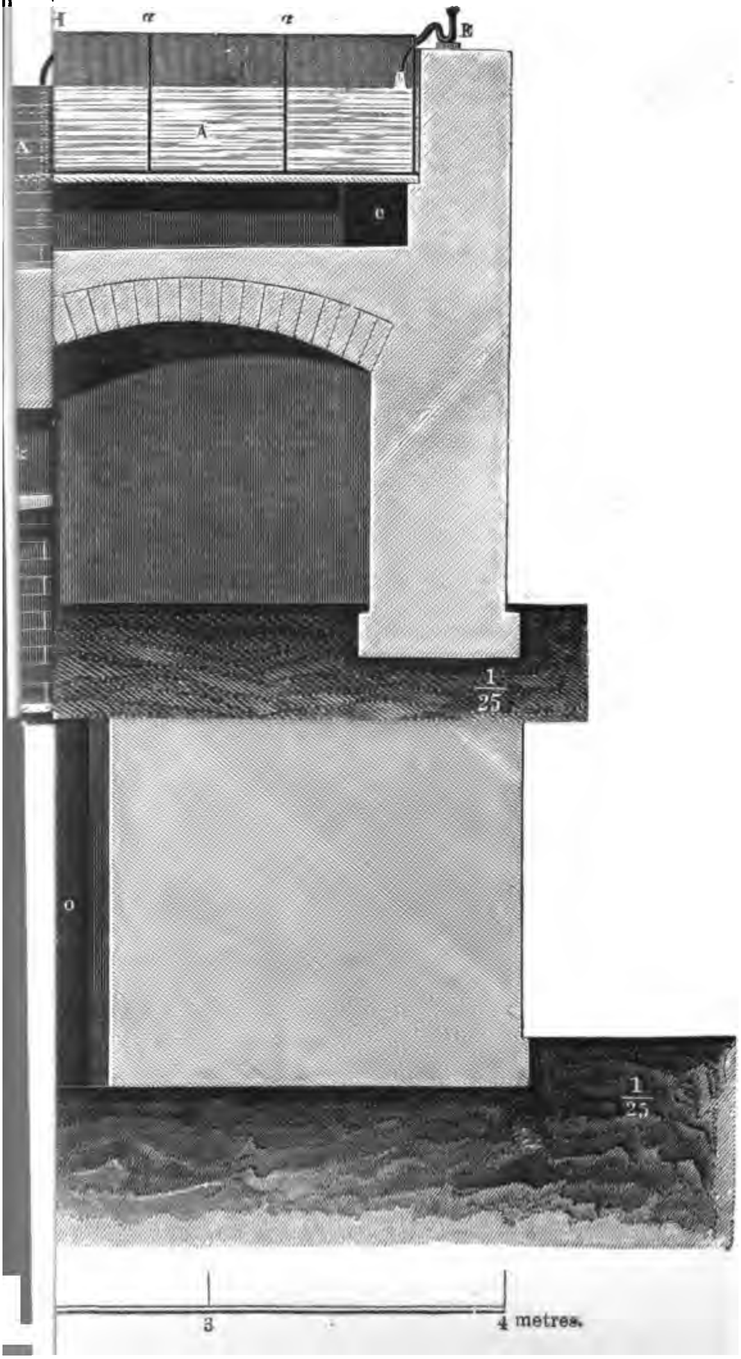
If the precaution be taken of replacing all the carboys by new ones after the lapse of six weeks, whether they seem damaged or not, there is next to no breakage of carboys, and the cost of concentration is reduced to 7*s*. 6*d*. per ton (Hofmann's Official Report, 1875, vol. i. p. 188). With this should be compared the very much higher cost for wear and tear of the platinum stills (to be given below), and, on the other hand, the much higher statement by Payen (p. 520) concerning the breakage, which, however, refers to the imperfect retorts of former times. Payen states that at Tennant's works at Glasgow only seven retorts, on an averag per annum. These retorts are made (by Perceval, Vick Co., of Manchester) from green soda glass, as even in t as possible, blown with special care, and cooled very slowl weight is about 60 lb. each, and they cost 1*s.* 4*d.* per lb.

Concentration in Platinum vessels.

The former arrangement of platinum apparatus, includi lead pans heated by the waste heat (see above, p. 499), is sented, after Schwarzenberg, in figs. 255 to 257.

The first four pans are heated by a special fire, whose shown at *b*, and its grate at *c*. After ranging along the bot the first pan, the flame is carried by the wall *d* under th half of the three other pans; it then returns to the front and goes through the vertical shaft *f* into the chimney. Fr last pan the acid passes into the platinum still B, of whi largest diameter is 2 feet 9½ inches; its height up to the ma on which the head rests, is 1 foot 7¾ inches; and it has a ca of 40 gallons. The whole lower part, which is continued an inch above its greatest diameter, is made in one piec upper part, narrowing towards the head, is gold-soldered bottom part by means of the oxyhydrogen blowpipe [l soldered with platinum itself, see above]. The remaining are made in a similar way. The still is heated by the firep At first it used to be set on an arch, only the sides being ex to the fire. On account of the great waste of fuel, the arc exchanged for iron bars; and as these burned away very qui the bottom of the pan was exposed to the direct flame. It not waste more quickly now than previously; and much less is consumed. The still is supported all round by the circular *l*, and, on account of the small strength of the platinum, also the middle wall *m*. The flame circulates in the flue *n* round sides of the still, and passes then under the fifth lead pan, a thence through *o* into the chimney. The projecting part of t brick covering of the flue *n* is protected by a metal plate extendin 4 inches upon the still; this plate, as well as the part of the sti not encased in brickwork, is covered with clay to prevent th condensation of vapours—which increases the production and saves fuel. The grates as shown in the diagrams are intended for lignite; for coal they can be made much smaller.

[*To face page* **526.**



The boiler is fed by the siphon *p*, one of whose ends dips into the lead pan, the other end dipping into the small lead vessel *q*, provided with a spout. The speed of flow is regulated by raising or lowering *q* by means of the chain running on the sheave *r*. The acid runs through the platinum funnel-tube *s* into the still, which is provided with a short neck and tight-fitting cover for receiving the same. The bottom of the funnel-tube is luted by the acid of the still; and a small box between the pipe and the opening of the funnel further prevents any vapour from escaping. For this purpose it has two partitions, one allowing communication only at the bottom, the other only at the top, and both together forming a complete acid lute.

A platinum float, playing in a similar tube to that of the funnel, indicates the level of the acid. The head C is let into the wide neck of the still, with the flange soldered all round it; the latter rests on the strong neck of the still, with a thin layer of asbestos between them, the two being pressed together air-tight by iron screw-clamps. The side branch of the head is fixed to a lead ball D by flanges, bolts, and red-lead cement; to the ball D a lead worm is burnt for condensing the weak acid distilling over; and the latter is collected in the lead tank E. The cooling-tank F is of lead, the frame for holding the worm of tinned iron. Cold water constantly runs in through *u*; and the hot water runs off at *v*.

The strong acid is drawn off through the platinum siphon *w*, reaching almost to the bottom of the still; the other branch passes through the cooler G, where cold water runs constantly in at the bottom and the heated water runs off at the top. To facilitate the cooling, the part of the siphon within the cooler is made in two branches, joined by cross stays; at the bottom is a gold tap for regulating or stopping the flow of acid; this tap is at least 20 inches below the bottom of the still. Two small funnels, *x*, fitted with ground platinum stoppers and rising above the top of the siphon, serve for charging it; for this purpose the bottom cock is closed, both funnels are opened, acid is poured in till the siphon is quite full, the air escaping through the second funnel, and the stoppers are put in. The siphon is usually made in four pieces ground tightly into each other at the joints, for the sake of being carried and handled more easily; screw clamps make the joints more secure; *y y* are wooden supports for the siphon.

The work of concentration goes on day and night, one man attending to both fires. The lead pans, whose area ought not to be smaller than that indicated, can easily concentrate the whole of the acid from 112° to 152° Tw. without any appreciable loss of acid. The weak acid runs into the first pan in a continuous stream of such amount that it is just balanced by the water evaporated and by the acid running from the fifth pan into the platinum still. The acid in the fifth pan is at the right strength when marking hot 132°; it will then mark cold 152° Tw. It is put into the still up to its widest diameter, and kept at the same height during the concentration by constant feeding.

The concentration may be carried on in two ways, either continuously or intermittently. When working continuously, the tap of the siphon is opened so far that the quantity of vitriol which the still can supply runs out in an uninterrupted stream, whilst from the lead pan just as much fresh acid runs into the still as keeps up the level, observable by the float. The process is controlled by noticing the strength of the acid running out of the siphon and of that condensing in the lead worm, both of which are in constant relation to each other. The distilling acid ought never to fall below 45° Baumé=90° Tw., in which case the concentrated acid will show 65½° Baumé=1·830 sp. gr. It is not very well possible to make stronger acid by the continuous process, because the constant supply of weaker acid keeps down the strength of the contents of the still. If the distilling acid shows less than 90° Tw., the acid flowing out of the siphon will soon become too weak; and in that case either the fire must be increased or the supply of weak acid must be lessened or even interrupted for a short time.

The apparatus as drawn here can supply 34 cwt. of strong vitriol daily by continuous working.

Acid of more than 1·830 sp. gr. is made by intermittent work. The tap is kept closed, till the distilling acid shows 100° Tw.; at this point the supply of fresh acid is stopped, the fire is drawn out of the grate, and a portion of the contents of the still is quickly drawn off into jars, but never so much that the level of the acid sinks below the fire-line at *n*. Each time 2 cwt. can be drawn off. The still is now refilled from the fifth pan, which for this purpose is temporarily disconnected from the fourth, lest weaker acid should get into the still. Once every 96 minutes, or 15 times daily, acid can be drawn off altogether, therefore 30 cwt. of acid of 1·840. It is evident that the interruption of firing during the drawing-off causes a loss in the amount of work done.

If real monohydrate (or something near it) is to be produced, the operation must be continued till the distillate shows the same strength; but this requires a much larger expenditure of time and fuel and great wear and tear of the still; it is therefore rarely done, although the "extra-concentrated vitriol" thus produced commands a higher price (see p. 517). Most of the acid is now prepared by the continuous process, which requires less fuel and causes less wear and tear of the still, in consequence of the temperature always remaining at the same height.

The acid is first run into jars of stoneware J, each holding 22 lb. of it, which stand on a lead saucer for catching any overflow; it is left in these several hours to be completely cooled before filling the carboys.

The acid distilling off is much purer than ordinary chamber-acid, and can be applied to special uses; otherwise it goes back into the chambers. The loss by evaporation, spilling, &c. ought not to exceed 1 or 2 per cent. The above-described apparatus requires daily 11 cwt. of good coal.

An idea of the size, working-capacity, and price of other platinum apparatus than that described by Schwarzenberg is given by the following statements (partly from Kerl-Stohmann's 'Technische Chemie,' iv. p. 1457). A still at Oker was 2 feet 11 inches in upper diameter, 2 feet 8 inches in lower diameter, 1 foot 5 inches in height, weighed with appurtenances 3 qrs. 4 lb., contained 66 gals., supplied daily 3 tons 2 cwt. of vitriol, and cost about £2000. A still at Freiberg had a diameter at the bottom of 3 feet 4½ inches, in the belly of 3 feet 7 inches, in the neck of 1 foot 1 inch, height up to the belly 1 foot 5½ inches, total height 2 feet 6 inches, weight with appurtenances 1 cwt. 27 lb., contents 88 gals., supplied daily about 3 tons acid, and cost £2800. Another apparatus weighed—the still 1 cwt. 27 lb., the head 4 lb., the side tube and float 4 lb., the float 22 lb., altogether 1 cwt. 2 qrs. 1 lb.; it furnished daily 4 tons of acid of 1·840 working intermittently, or 6 tons of 1·83 working continuously, and cost about £3200. The daily cost of interest and wear and tear is stated at 19*s*. The price of platinum has gradually lowered: in 1857 it was 1200 francs per kilog. (=£21 17*s*. per lb.); in 1872, only 750 frs. (=£13 13*s*. per lb.); in 1877, 1020 frs. (=£18 11*s*. per lb.).

Bode (Dingl. Journ. ccxxi. p. 543) states the following weights and working-capacities of some platinum stills, from his own experience:—

Weight of platinum, inclusive of all appurtenances. cwt.	qrs.	lb.	Quantity of strongest oil of vitriol per 24 hours. tons.	cwt.
1	2	8	7	5
0	3	6	3	15
0	3	2	1	19
1	0	16	5	0

In consequence of competition with the platinum stills, first by the improved glass retorts, and more recently by the combined platinum-lead apparatus of Faure and Kessler, the two manufacturers of large platinum apparatus (Desmoutis, Quennessen, & Co., of Paris, and Johnson, Matthey, & Co., of London) have both greatly improved the construction of platinum stills. Especially, they have made them lighter, by leaving the greatest strength entirely in the bottom, directly exposed to the fire. Already in 1867, Johnson, Matthey, & Co. had exhibited at Paris an apparatus for 5 tons per diem, costing only £1640, and another for 8 tons per diem at £2500. Their apparatus are represented in figs. 258 and 259. The first

Fig. 258.

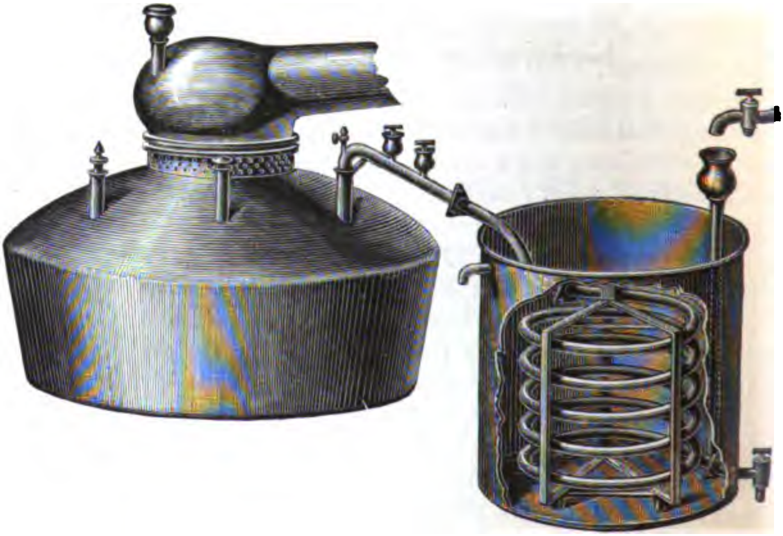


Fig. 259.

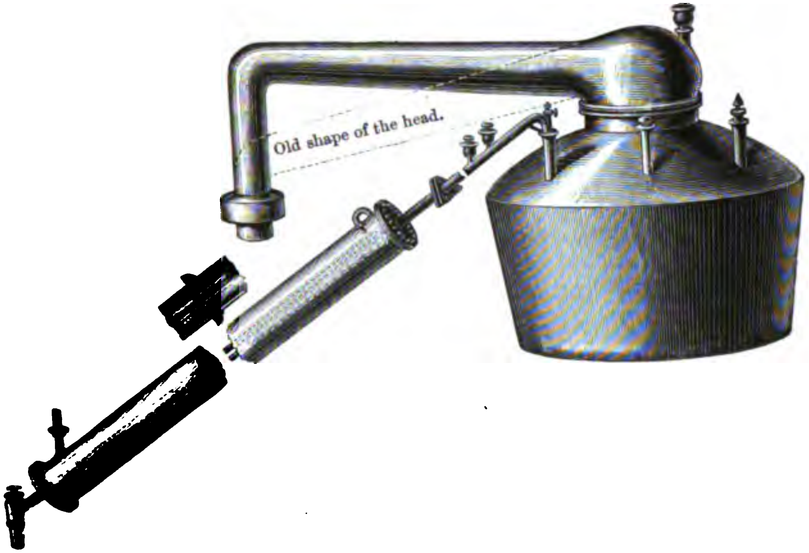
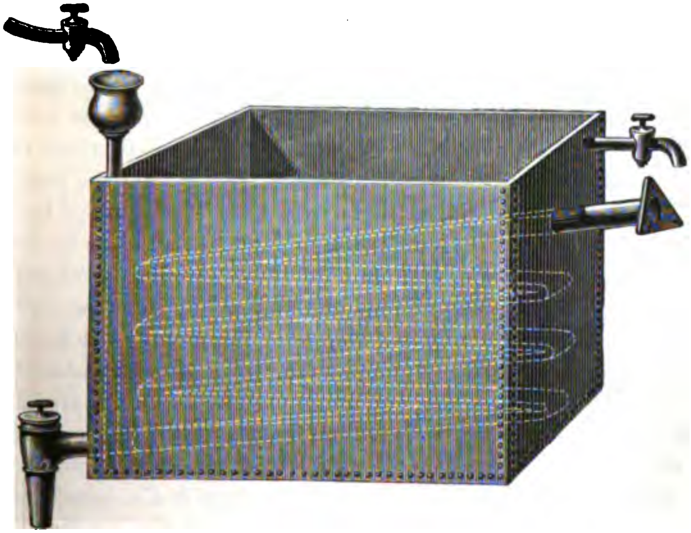


Fig. 260.



shows the flat shape, the second the tall shape of stills; in the latter the head first rises a little to allow the weak acid, condensing at first, to run back again into the still (the dotted lines show the older shape of head, still usual in the French apparatus). With the English construction of the still-head less weak acid is obtained, but less work is done, than with the French apparatus. Fig. 260 shows a cooling-apparatus of peculiar construction, sometimes employed in the English apparatus.

The lightest construction of English platinum stills, where only the bottom is heated, and which, since 1876, has been most recommended, is shown in fig. 261, along with a new cooling-apparatus. Such a still was exhibited at the London Exhibition of 1862, and since that time has regularly made upwards of 2 tons of vitriol per diem; it originally cost only £675, inclusive of head, tubes, and cooler; and the repairs during 14 years have only amounted to £30. This system is meant for continuous work; when two stills are combined, 4½ to 5 tons, with three stills, 7½ to 8 tons of vitriol can be produced per diem; but in that case the cooling-apparatus must be enlarged accordingly. A double apparatus costs £1200, a triple one £1750. A is the platinum still itself, with an ascending head L; it rests on a cast-iron ring C, and is heated by the fire on the grate *c*; below the latter there is an ash-pan filled with water. In the centre of the still-bottom is a funnel D, communicating with the outside by the connecting-tube E; the concentrated acid collects here and is carried away by E. This arrangement is said to have been a great practical success. The tube E is continued into another platinum tube, dipping 2 inches into the funnel of the platinum cooler F. The latter stands in a lead cooler G, which constantly receives fresh water from a tap; the pipe conducting the cooling water to the bottom of G is surrounded by spun yarn or some other bad conductor of heat, so as not to be heated prematurely. From the bottom of F the acid, already cooled to a great extent, runs through an overflow-pipe (likewise wrapped round with spun yarn, to avoid reheating the acid by the hot water in the upper strata) into the stoneware cooler H, which also stands in a cold-water tub. The siphon I, of lead or stoneware, draws the acid from H into the large stoneware bottle K, from which, now sufficiently cooled, it is drawn off by a tap as required.

In the same year (1876) Johnson, Matthey, & Co. constructed a totally different shape of still ("system Delplace"), in which Faure and Kessler's idea of working with a very thin layer of acid, thereby permitting a diminution of the weight of platinum, is adopted; and it effects at the same time an enlargement of the heating-surface by

Fig. 261.

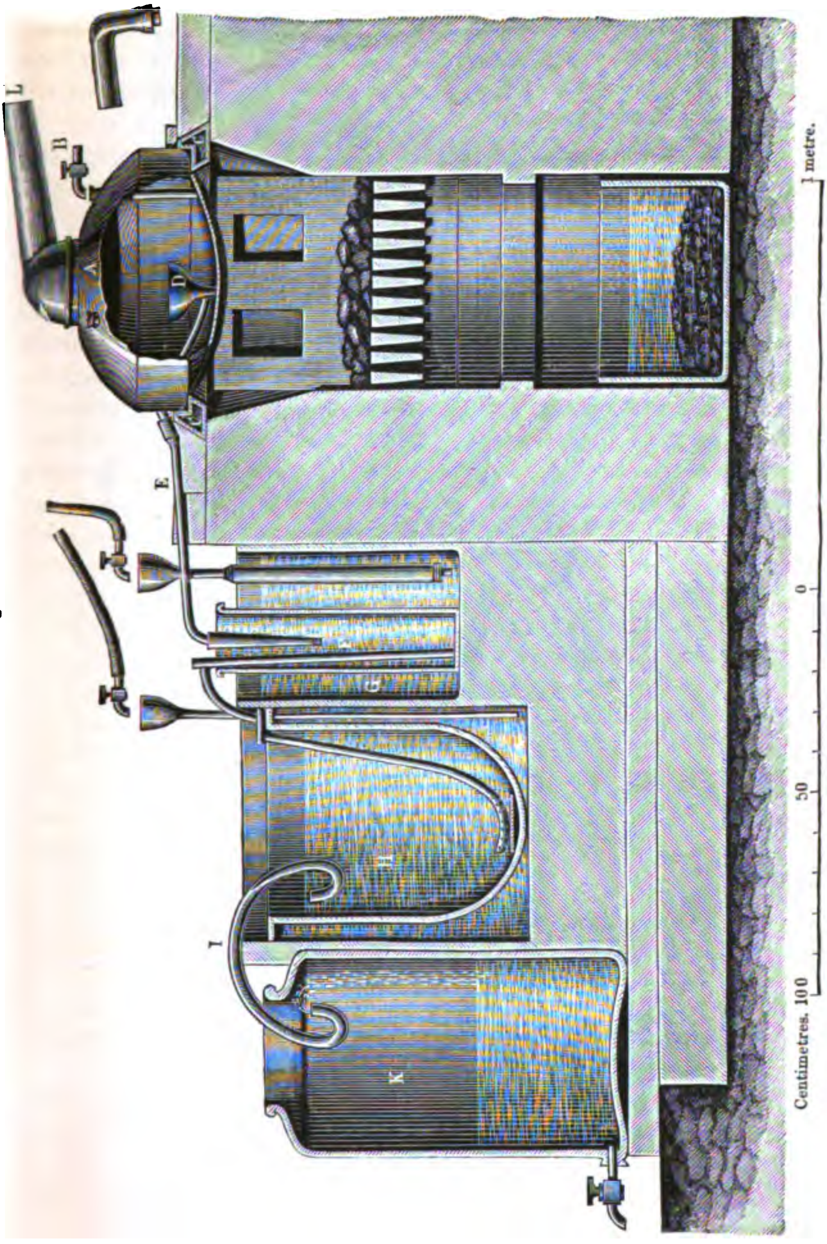
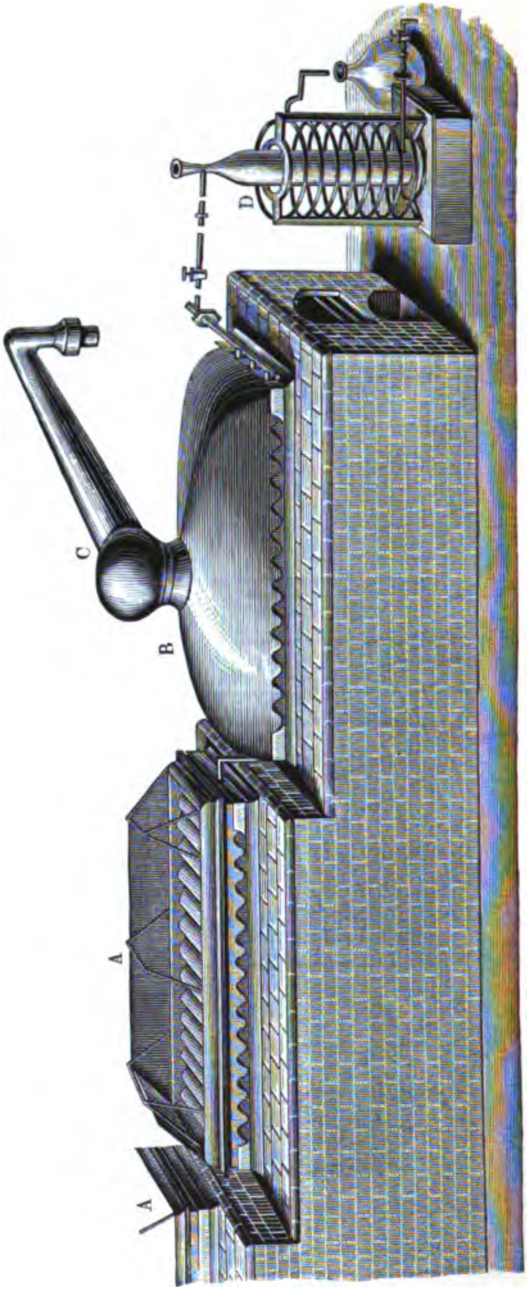


Fig. 282.



employing a corrugated still-bottom (Prentice's patent). This apparatus is shown in figs. 262–264. The still B, instead of being round, is of an elongated square or oval shape; for a make of 4 to 5 tons of vitriol per diem it measures 3 feet by 1 foot 6 inches. The acid enters at the back end and comes out in front; the siphon is replaced by an overflow. A still of this kind weighs about ½ cwt., and costs about £1000, inclusive of overflow, cooler, metal ring, &c. The firm also supplies platinum pans with corrugated bottoms, as shown at A; but instead of these, ordinary lead pans may be used.

More precise (and partly deviating) statements about these apparatus have been made ('Chemische Industrie,' i. p. 194) by the manager of the Griesheim Chemical Works, where three of them are at work. Each of them consists of a closed still, 2 feet 11 inches by 1 foot 5½ inches, and two open pans, 4 feet 1 inch by 1 foot 5½ inches, and 5 inches deep, the latter with a channel for a water lute running round the upper edge. The pans have a double lead

Fig. 263.

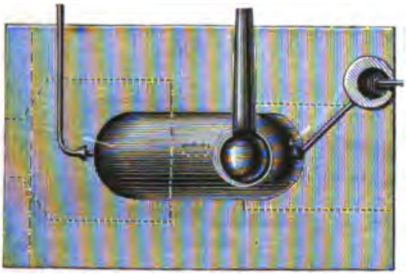
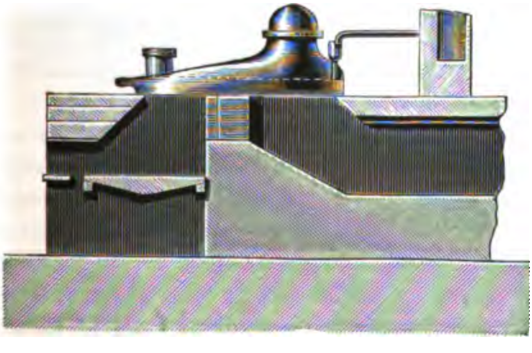


Fig. 264.



cover with cooling-water; the gas not condensed is taken away by a vertical lead tube into the outer air. The liquids condensing at the sides of this lead roof (water in the first pan, acid of 1·03 sp. gr. in the second) flow into the channel and run away.

Six lead pans, with a heating-surface of 247 square feet, belong to the system. The firing is done by gas-generators. The system concentrates daily 6 tons of vitriol of 1·843 from chamber-acid of 1·55, with a consumption of from 26 to 27 cwt. of Saar coals. The acid in the lead pans reaches a temperature of 125°–135° C., and a strength of 1·68 sp. gr. (measured at 15°), in the first platinum pan 195° and 1·74, in the second 240°–250° and 1·81 sp. gr.; the thermometer under the roof of the first pan shows 90°, under the second 130°. The distillate of the still proper has a specific gravity of 1·45. The still, inclusive of all accessories, weighs 1 qr. 12 lb., each pan 20 to 22 lb. The apparatus is said to be very satisfactory, and simpler than Faure and Kessler's [to which it bears a very great resemblance !].

The more modern construction of Desmoutis, Quennessen, and Lebrun, of Paris, is shown in figs. 265 and 266. The still A has the head B projecting a little over its neck. The acid is continually supplied through the funnel (with lute) *a*, and is divided into small drops by the holes of the still-neck *p* in the part reaching into the still-head. These drops run down the sides of the still, and are concentrated to some extent before they arrive below. At *o* the flow is put in. The siphon (according to Hasenclever's plan, 'Berichte der deutsch. chem. Gesellschaft,' 1872, p. 507) is

Fig. 265.

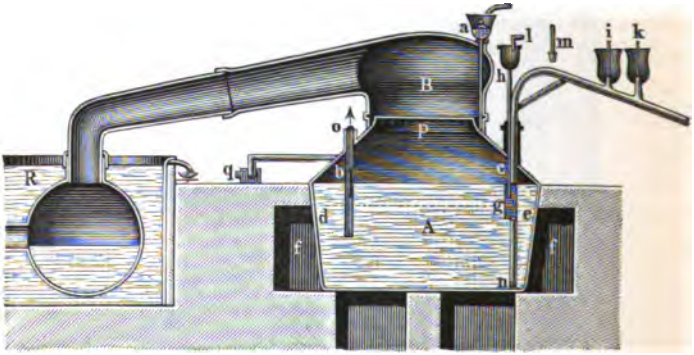
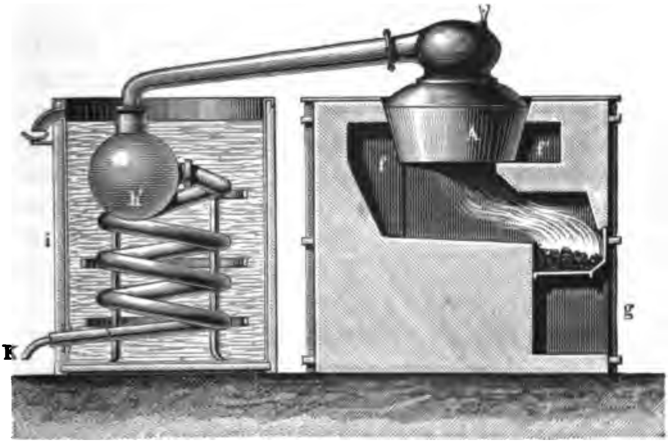


Fig. 266.



made in this way:—Lest through a mistake of the attendant too much acid should be drawn off and its level fall below the line *d e*, thus exposing the platinum to the heat of the flue *f f* without any protection from acid inside, and causing it to become red-hot and perhaps to crack, a small tube, *g h*, is fixed in the siphon, whose lower opening corresponds with the lowest allowable level of the acid in the still. When the liquid stands above *d e*, the opening *g* is covered and the siphon acts as usual, drawing off the concentrated vitriol from the bottom of the apparatus; but whenever the level of the acid sinks below *d e*, the siphon sucks air at *g* and runs off. The funnels *i* and *k* serve for refilling it. If, exceptionally, the still has to be emptied, the cover *l* is taken off, the plug at *h* is put in, and the acid can then be siphoned off down to *n*. The overflow *q*, on the other hand, always keeps the level of the acid below the line *b c*. The vapours escaping from the head B pass into the lead ball in the cooler R, which is always half-full, as the worm of the cooler starts from the middle of its height; this prevents the acid from dropping down and wearing out the lead too soon at the point of contact. At S the condensed weak acid runs off. The siphon, whose long arm is a plain tube cooled by water, takes the concentrated vitriol into a set of from four to six jars with open necks, standing up to their necks in cold water, and connected one with another by glass siphons; from the last of these the acid is drawn off into carboys by means of a platinum siphon with stopcock. Thus the acid, besides being cooled, is at the same time clarified.

These deep stills are still used in many places; but the Paris firm, since 1876, in order to compete with Faure and Kessler's apparatus, has brought out a new form of still, which, similarly to that of the London firm, has for its object easier concentration by diminishing the depth of the acid, along with a saving of fuel and diminution of the weight of platinum. The apparatus (figs. 267 and 268) is filled at *a*; the acid is compelled by concentric partitions to travel through the stills in three circles, following the direction of the arrows; it is taken away from the centre by the tube *b*, without a siphon. In a convenient place there is an overflow, to prevent the level of the acid rising too high. The still is either set on brickwork in the ordinary way, or it is made with a recess near the outlet-tube for resting on the brickwork. Bode states that an apparatus of this kind, supplying daily 1½ ton of the strongest vitriol, weighed:—

Fig. 267.

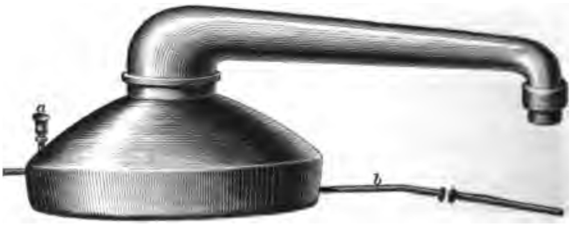
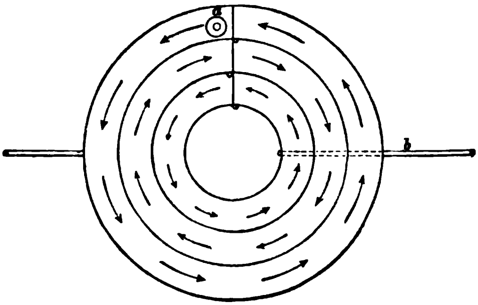


Fig. 268.



	grms.
The still itself	11935
„ head	2784
„ funnel	244
„ overflow and run-off......	203
„ siphon [what for?]	2429
	17595

[=38¾ lb.]

According to a circular of Messrs. Desmoutis, Quennessen, and Lebrun, an apparatus of 2 feet 7½ inches diameter, weighing ½ cwt.,

Fig. 269.

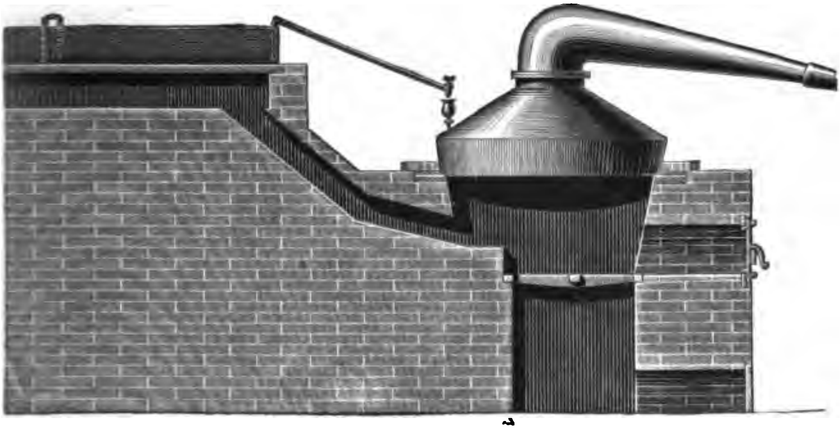
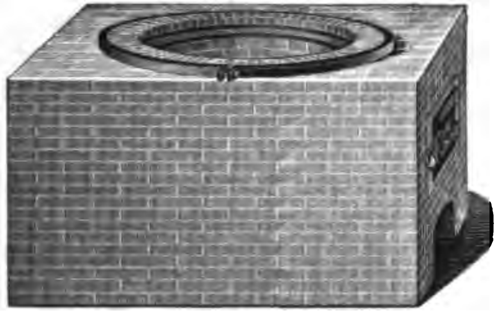


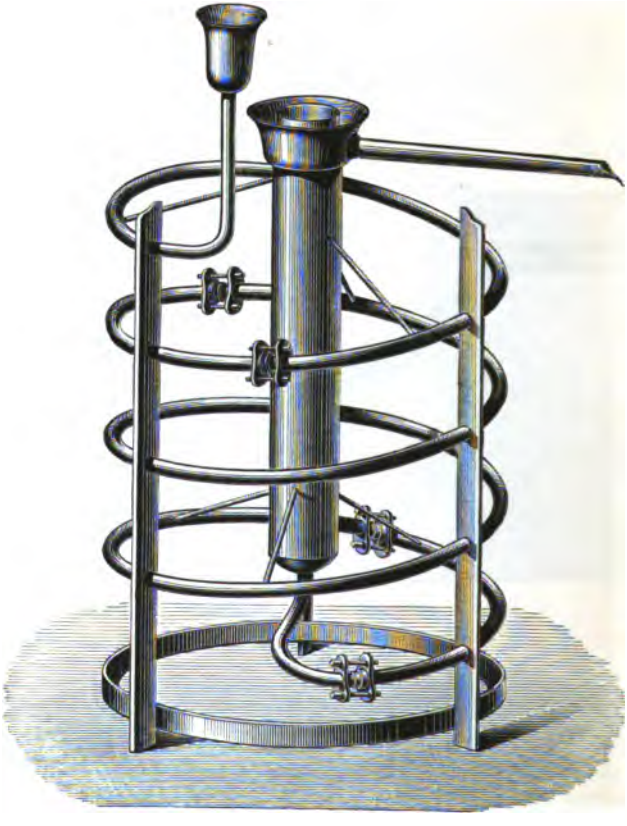
Fig. 270.



can easily furnish 4½ to 5 tons of strong vitriol daily, with a maximum consumption of 16 parts of coals for 100 parts of acid; this consumption is now said to have been reduced to 13 parts.

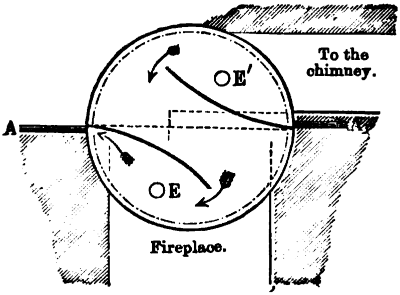
The kind of setting now used at most works is shown in figs. 269 and 270. It is extremely simple, the still-bottom resting on a cast-iron flange. The Paris firm also supplies a cooler (fig. 271) similar to the English cooler (fig. 257). Three such apparatus are at work at Chauny; the distilling acid is said to reach only 6 to 8 degrees Twaddle.

Fig. 271.



The above-described mounting on a plain cast-metal ring was first suggested by Mr. Schaffner, of Aussig, seemingly also the idea of combining the principle of the shallow pan of Faure and Kessler with a platinum head, thus uniting the advantages of both systems. Bode has proposed to run in the acid at the centre, and run it off at the circumference (so that the run-off tube would not have to be carried right through all the partitions), and not to reduce the depth of the acid too much. Another system for circulation of the acid, introduced by M. Liebig, is sketched in fig. 272.

Fig. 272.



Double outflows A A, and supply-tubes E E, one of which is always closed by a cap, permit the still to be turned from time to time, so as not to have always the same place in contact with the fire. The second supply-pipe may be utilized for holding a float. The cooling is effected by a platinum worm. His apparatus, measuring 2 feet 5½ inches at the bottom, weighs 54 lb. (the cooling-worm another 5½ lb.), and supplies daily from 3½ to 4 tons strong vitriol. Liebig prefers the ascending still-head, according to the English pattern; the distillate condensing in it shows 140° Tw., and is carried away to the supply-tube by a small contrivance inside the still-head (Post, 'Zeitschrift f. d. chem. Grossgewerbe,' i. p. 88).

In the stills supplied by the Paris firm, as last described, the depth of the acid is only from 2 to 3 inches; with good work the distilling acid shows no more than 7° to 9° Tw., even when vitriol of 1·842 sp. gr. is made; the work done is now five times as much as formerly for an equal weight of platinum.

Schaffner has simplified the cooler extremely. He uses a simple siphon without a stopcock (the outflow being regulated by the supply); the acid runs directly into a cylindrical tank of thick lead, 2 feet wide and deep, to the bottom of which a lead pipe is joined, turning upwards again, just as in his cooler for Glover-tower acid (p. 406). But in this case, on account of the greater heat of the acid, there is a *double* lead worm for continually running cold water through the tank. The acid running off is quite cool, so that the carboys may be filled directly. The cylinder has a lead cover to protect the acid from discoloration by dust.

We have several times already mentioned the concentrating-apparatus of Faure and Kessler; we will now describe it in detail. The following is the principle of the apparatus (invented by Kessler): of the platinum still nothing is left but the bottom, forming a shallow dish, the remaining part being replaced by a lead cover cooled by water. The first construction of this kind was proposed by Kessler in 1863 (Dingl. Journ. ccxxi. p. 85), and carried out at Griesheim, near Frankfort (described in detail, Dingl. Journ. clxxvi. pp. 34 & 164), but was not, in the long run, a success. Messrs. Johnson, Matthey, & Co. have proved that even before 1860 two British manufacturers (Messrs. Harrison, Blair, & Co., of Bolton, and Mr. A. Smith, of Dublin) had used similar pan-apparatus, but had given them up again. On that very account, Faure and Kessler cannot be denied the merit of having ultimately carried out in practice a principle all previous attempts to apply which had failed; and even if, as it seems, the modern constructions of the the stills made entirely of platinum are after all the best apparatus of the kind, Faure and Kessler have certainly, by their original improvements, induced the older manufacturers to follow their example.

The older forms of the apparatus (now given up by the inventors themselves) are described in Dingl. Journ. ccxi. p. 26, and ccxiii. p. 204); we here describe only the form ultimately adopted and introduced in many places. Fig. 273 gives a section, fig. 274 a perspective view, and fig. 275 the details of the joint between the dish and the jacket (according to 'Engineering,' Feb. 25, 1876). For a complete apparatus two platinum dishes, A and B, are required. They are circular, 2 feet 4½ inches wide at the bottom, and 5 inches high; they are mounted in such a way that the acid runs from the first dish, A, through the platinum tube *a*, into the lower dish, B.

Fig. 273.

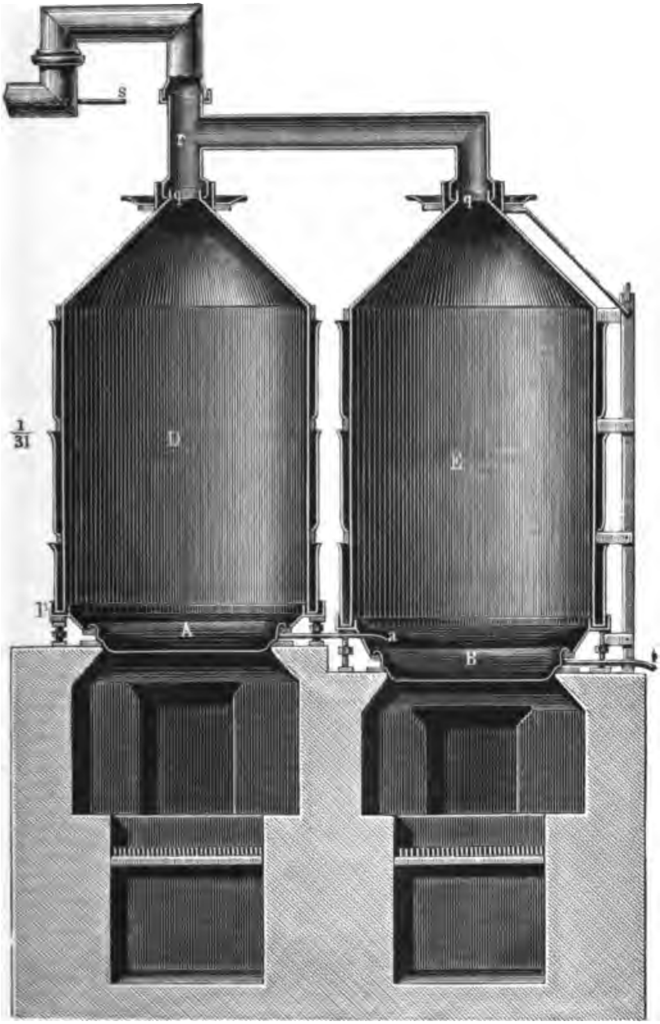


Fig. 274.

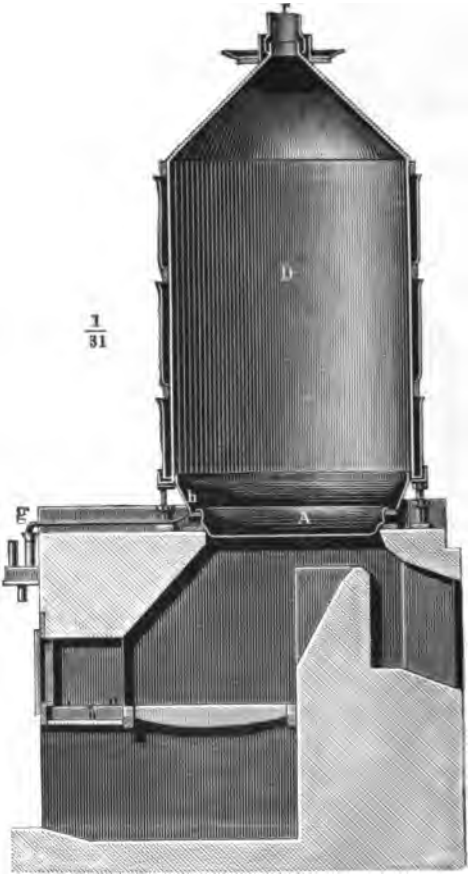
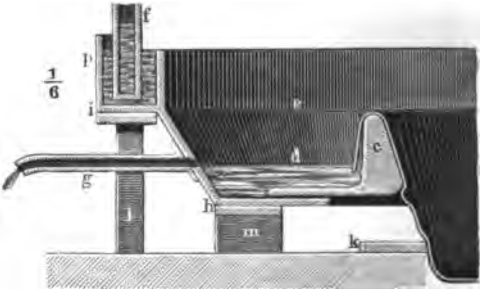


Fig. 275.



Each dish is fired independently, hanging freely in the fire-place, merely supported by a metal ring, *k*, which itself rests on the brickwork. The rim of the dish is recessed for this purpose; it is supported above by a thick lead ring with a vertical flange, *c*; there is no cement between the lead and platinum, the air passing freely through. The flanged lead ring *c* is burnt to another circular lead piece, *h*, called the "soubassement," which turns upwards in a slanting direction, and then carries two concentric lead flanges, forming an annular water lute *p*, into which the lowest part of the hollow lead bell *f* dips without touching the bottom. The iron rings *i*, with 6 adjustable feet, *l*, and the wedges *m* support the soubassement. The small overflow-pipe *g* constantly takes away the weak acid collecting at *d* in the soubassement. The lowest ring may be left out, and the lead rest directly on the brickwork. The lead bells D and E are 4 feet 3 inches high, and 3 feet 6 inches wide, and have a circular water-jacket in three tiers. Between each two tiers an iron hoop is laid round the bell to stiffen it; and at the same time to these hoops are attached the pieces by which the bells are suspended from the vertical supports carrying their entire weight. The bell ends at the top in a conical cover with a short tube-like opening, *q*, in the centre; round this a water-joint is formed, in which the lower part of the tube *r* rests, which takes the uncondensed vapours to the chambers. [In practice the vapours are generally not carried into the chambers, but condensed separately.] A steam-jet at *s* causes air to be constantly aspirated between the lead piece *c* and the dish-rim at *d*, and thus assists in taking the vapours away from beneath the bell. A stream of water runs over the conical bell-cover continually, flows into the upper annular jacket-space, from this into the second, and then into the third, running away at the bottom, keeping the sides of the bell constantly cool, and condensing the vapours in it into liquid acid. This first enters the hydraulic joint at *p*, then passes over into *d*, and is taken away by the overflow-pipe *g*. The latter is fixed at such a height that the turned-over margin of the dish just dips into the acid, so that no vapours can get outside, whilst the aspirated air can get through.

The dish A is 5 inches above B; acid of 144° Tw. constantly runs into it through a platinum tube; it runs, partly concentrated, through the platinum tube *a* into the dish B, and from this, as strongest vitriol, through a third platinum tube, *t*, into the cooler to be described below. The process is thus quite continuous; but the largest part of the work is done in the dish A, which can be used by itself, of course with a smaller production. The dilute acids in the first bell show 7°–15°, in the second 52°–77°, on the average 32°–38° Tw. against 64° Tw. in the *older* platinum apparatus. The apparatus here sketched turns out 6 tons of strongest vitriol daily, with a consumption of 5 cwt. of fuel per ton of vitriol.

Bode gives the following authentic details on the consumption of fuel with Faure and Kessler's apparatus, compared with others (Dingl. Journ. ccxx. p. 336):—

I. An old platinum still consumes 2·34 cubic feet of wood per cwt. of vitriol—of this 0·98 for the lead pans, 1·36 for the still itself; the new apparatus at the same works only consumes 1·57 cubic feet.

II. In another case the consumption of fuel for concentrating from 106° to 170° Tw. was just the same as from 148° to 170° Tw. with the old apparatus.

III. For obtaining 38 cwt. of strong vitriol daily 7 cwt. of large coal are used; but a little under 4 cwt. should be deducted, as the warm cooling-water is used for feeding a steam-boiler, leaving only 10 lb. of coals for 1 cwt. of vitriol; the old platinum apparatus had consumed 6½ cwt. of coals for 38 cwt. of vitriol. The dish here has a diameter of 2 feet 1½ inch, weighs, along with the other platinum parts, 20 lb., and costs £460, including royalty, but without the cost of lead, mounting, &c.

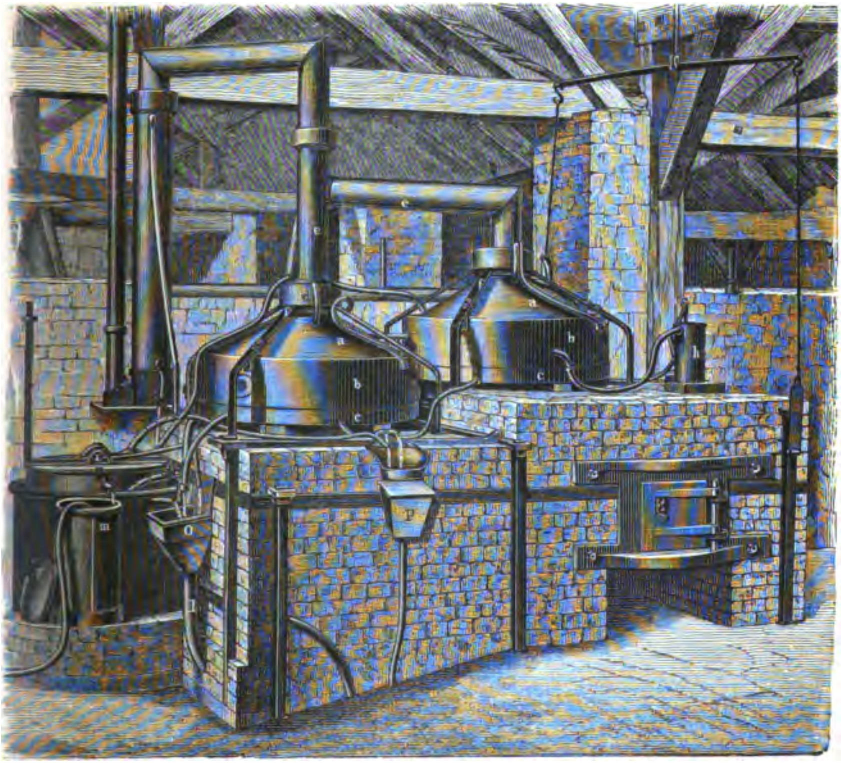
IV. Here for 100 parts of acid, concentrated from 106° to 170° Tw., 30 parts of good coal are used.

According to Payen's 'Chimie Industrielle' (1877), i. p. 341, from 18 to 20 kilog. coal are used for obtaining 100 kilog. of strong vitriol from acid of 106°–113° Tw. According to notes collected quite recently by the author, chamber-acid of 113° can be brought up to nominally 170° Tw. (=94 per cent. of SO_4H_2) with 16·6 parts of middling good coals for 100 parts of strong vitriol.

It should not be overlooked that the cooling of the bell in Faure and Kessler's apparatus requires a very large quantity of water, which in some places may militate against its employment.

The shape of the bells as drawn, 4 feet high, with three tiers, is not at all the general one; shorter bells, with only two tiers, sometimes even in one piece, have also, recently especially, come into use. Fig. 276 (also from 'Engineering') gives a perspective view of such an apparatus. *b b* are the bells (only 1 foot 4 inches high),

Fig. 276.

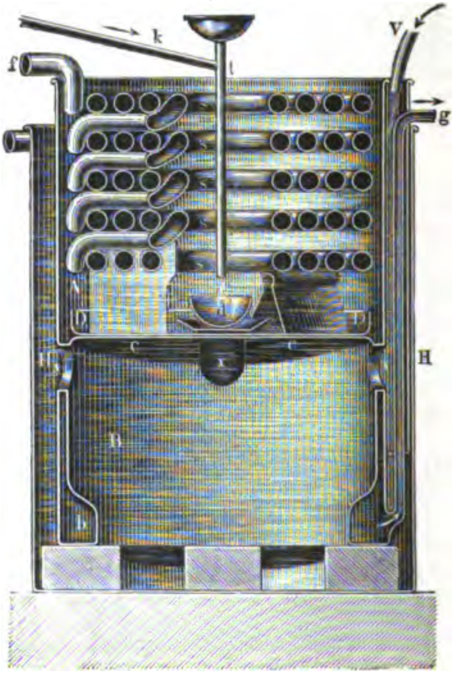


a a the conical tops with the water-joints *d* and the drawing-off tubes *e, c* the hydraulic joint of the lead rim, *f* the iron bearers of the bells, *g* the supports of the lead rim, *h* a pot with hot acid of 144° Tw. from the pans, *n* the cooler for hot strong vitriol, *m* a collecting-tank for the acid, *o* a collecting-box for the different cooling-waters running off through the pipes *l* &c.; through *k* and other pipes the weak condensed acid runs into the collecting-funnel *p*. This apparatus has two dishes of 2 feet 6 inches diameter, and supplies 7 tons of strong vitriol daily.

Faure and Kessler's apparatus is also specially adapted for vitriol of 1·840 sp. gr., and even for the "extra-concentrated acid" of 97 to 98 per cent. In this case the weak distilling acid in the second dish shows from 124° to 144° Tw., and there is a loss of platinum of 8 to 9 grams per ton of acid: the average strength of the distilling acid from both dishes is 52° Tw.

The cooler employed by Faure and Kessler was also constructed by them; it is made of lead, avoiding the use of platinum, similar to Schaffner's. Its best form is shown in fig. 277 (from Payen, *l. c.* p. 341). A lead vessel, A, stands on an annular lead cylinder, B, whose base *b* is a little widened out for greater stability. In the middle of the height the partition *c* cuts off the top from the bottom cylinder, the hollow space of A still remaining in communication with the annular space of B. All the hollow spaces are filled with vitriol. On the bottom *c* the shallow lead dish D is placed; and in its centre the porcelain dish *d* receives the almost boiling acid from the platinum tube *k*, so that the hot acid mixes with cooled acid without injuring the lead at the point of contact. In A there are five worms, *s s*, connected with each other and con-

Fig. 277.

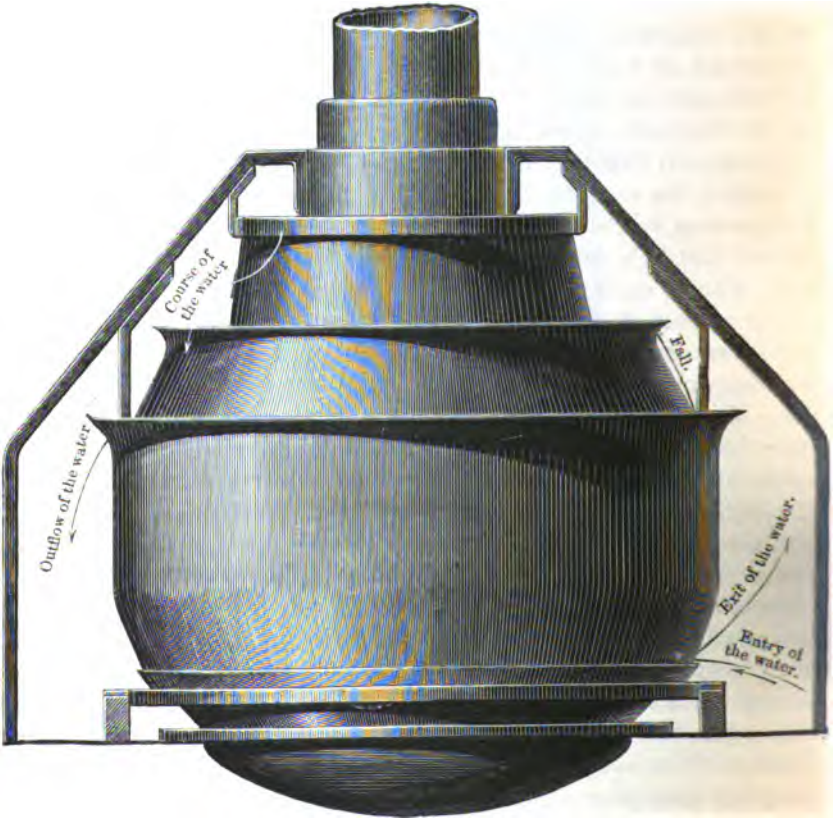


stantly fed with cold water, which runs off heated at *f*. The whole cooler stands in a cylindrical vessel H, also constantly supplied with cold water through V; the latter, therefore, always fills the inner space *b* of the annular vessel B, circulating through the openings *x x*. Since the acid entering through the tube *t* is much hotter than that into which it flows, it rises to the top, comes into contact with the worms *s s*, and is partly cooled; it then flows downwards along the sides, and passes into the annular space *b*, where it only forms a thin layer and is further cooled. At last it rises up in the pipe *g*, and from this runs into the carboys. As the diameter of the vessel is about 3 feet 3 inches, the stream of acid moves very slowly in it, and there is time for cooling. A cooler of the above diameter and equal height suffices for 100 carboys of acid per diem. This apparatus is very ingeniously constructed, but rather complicated. It requires an excellent plumber and incessant cooling with cold water; otherwise it would be very soon destroyed.

The use of Faure and Kessler's apparatus spread very rapidly, and far more in Germany and Austria than in France itself, last of all in England—up to 1877 altogether in 40 works. The reason was evidently this, that, in spite of the very large royalty paid to the inventors, the saving against the *older* platinum stills amounted to a large sum, so that the cost of the old platinum equalled that of two of Kessler's new apparatus. The latter for 5 tons daily costs only £1200, against £3200 for the old still, or for 2½ tons daily £600 against £1800 [these figures quoted by F. & K. were certainly *maximum* amounts]. Besides, with the new system less fuel was consumed. But, as mentioned above, the firms of Johnson, Matthey, & Co., and Desmoutis, Quennessen, and Lebrun have both come up to the same point; they now supply apparatus at the same price as Faure and Kessler, or even more cheaply, which have the great advantage of consisting entirely of platinum, and thus always retaining the best part of their value, and of being much simpler to mount and to keep up. The principle of a shallow layer of acid being adopted, they attain the same saving of fuel, and even exceed it if constructed on the principle of the concentric current—though this principle can be, and actually is, applied to Kessler's platinum dishes also. In some places the dish-apparatus is said to have been abandoned again, probably on account of too many repairs being needed. It can be very easily imagined that in one place, where a less-practised plumber has mounted the apparatus, it works much less satisfactorily than in another place, where there has been an excellent plumber at disposal; at least in some places the author has been told that there was no difficulty whatever in keeping the apparatus in good order.

The greatest advantages claimed by Faure and Kessler for their apparatus are its cheapness and the saving of fuel—advantages which the apparatus even at the time of its introduction hardly possessed against the apparatus of Johnson, Matthey, and Co. of 1862, and which it has entirely lost against the most modern platinum stills, at any rate so long as a very high royalty (amounting to the value of the platinum itself) has to be paid for it. The other advantages claimed, viz. smaller loss in case of accidents, less

Fig. 278.

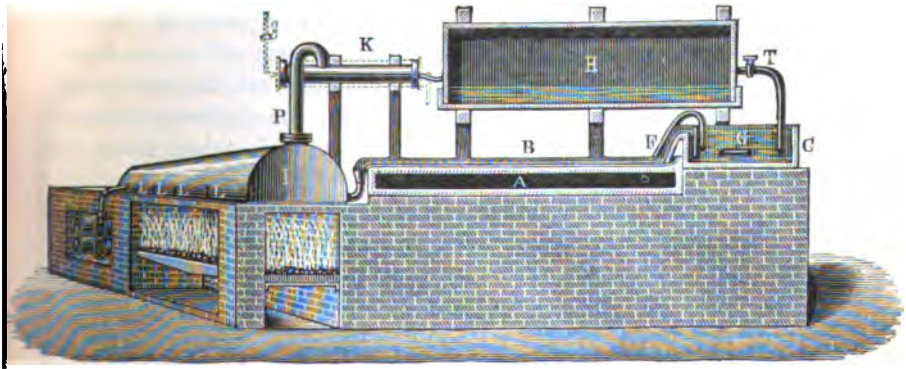


manual labour, greater regularity of work (?), smaller consumption of platinum, &c., all fall under the same head. The loose platinum dishes no doubt are more easily repaired than the close stills; on the other hand the lead parts give all the more occasion for repairs. The lead cooler of Faure and Kessler does not seem to answer completely; at least they also, latterly, recommend a platinum cooler. The distilling acid in the newest platinum stills is much weaker (as we have seen above) than that in the Faure-and-Kessler apparatus, which is in favour of the former. Lastly, the platinum stills also save all the cooling-water required in the other apparatus for the lead bells.

In a circular of February 25th, 1877, Messrs. Faure and Kessler describe some important improvements now introduced by them, without, however, giving any diagrams. The "soubassement" with double hydraulic joint, which gave frequent occasion for repairs, is abolished; the platinum dish is much higher and itself provided with an hydraulic joint; its sides are exposed and thus allow better joints to be chosen for the exit-tubes; there is an overflow-pipe, &c. The preceding diagram (fig. 278) gives an idea of this construction.

Bode reports (in Dingl. Journ. ccxxviii. p. 249) on a new platinum apparatus patented in Germany (No. 1005, 9th Oct. 1877) by F. W. Kalbfleisch, of London. The diagram (fig. 279) refers to this.

Fig. 279.



A is a shallow box with bottom and sides of sheet iron, and its top made of steel plate, set in asbestos mortar or some other badly conducting substance; it carries a shallow lead pan, B, into which the heated acid from C runs through a siphon F. The depth of acid in B is not to be above ¼ inch. The heating takes place by superheated steam; thus overheating of the pan by direct exposure to the fire is avoided, and thin sheet lead can be employed. The superfluous steam passes through G, and gives a preliminary heating to the acid in C. The remaining steam may be further used for heating the feed-water of the steam-boilers, and may be ultimately taken through T into the lead chambers. [The various steam-pipes certainly ought to be provided with suitable apparatus for carrying off the condensed steam.] The condenser K is connected with the platinum still I by an upright pipe P; this, as well as the higher situation of the condenser, is much insisted upon by the inventor. The condenser discharges its acid immediately into the lead chamber, H; this, however, is decidedly wrong, as the weak acid will always float at the top, causing the conversion of nitrous acid into nitric acid and quickly corroding the lead. Bode proposes, instead of this, to employ the steam for concentrating the distillate. Behind the platinum vessel the fire is in contact with pipes for overheating the steam, which is to be controlled by a pyrometer.

The platinum vessel is rectangular, with an oval cover, slanting backwards; the reason of this is, because the vessel is fed with acid in front over the outlet-pipe P, and most vapour is given off there. The whole bottom is directly exposed to the fire, and is supported internally by the cross girders L, soldered to the bottom and the sides and dividing the space into compartments, at the bottom of which the acid communicates and runs off concentrated at M. The outlet-pipe is bent for a hydraulic lute, the bend determining the level of acid within the vessel; the shallower the acid the more work is done. The acid drawn off is taken from the bottom as usual.

The consumption of fuel is stated at less than half that of the old platinum stills. A vessel of 2 ft. 1 in. × 4 ft. 2 in. area, costing below £1250 inclusive of cooler, is said to supply 7 tons 6 cwt. of strong vitriol in 24 hours with a consumption of less than 10 cwt. of coals = 6½ per cent.

Bode points out that the platinum vessel is difficult to clean, especially on account of the cross partitions. If the well-known ferric sulphate should be precipitated, weak acid must be sent through the vessel at a moderate heat; but no control can be exercised.

The idea of using the waste heat of the platinum still for superheating steam seems novel; but the arrangement for utilizing every thing to the utmost is extremely complicated and will hardly stand the test of practice without dropping one thing or the other. The vapours not condensed have been taken into the chamber already by Faure and Kessler; and this Bode prefers to condensing them completely to weak acid, at least when the chamber-gas has no pressure outwards, but suction inwards.

An important chapter in the concentration of vitriol in platinum is that treating of the *loss of platinum* by gradual solution in sulphuric acid. The first accurate observations on this subject were made by Scheurer-Kestner. He found (Hofmann, 'Report of the Juries 1862,' p. 16) that, even with perfectly pure sulphuric acid, the loss of platinum amounted to 2 grms. for each ton of vitriol; when nitrogen compounds were present in the acid, it rose to 4 or 5 grms. of platinum: this, however, can be avoided by purification with ammonium sulphate (p. 482). New stills lose less than old ones (about 1 grm.), because newly hammered platinum is more compact and resists the acid better. The iridium-platinum alloy of Desmoutis and Quennessen (25 to 30 per cent. of iridium) suffers less; in an experiment a dish of pure platinum lost in two months 19·66 per cent., another of iridium-platinum alloy under identical circumstances only 8·88 per cent. of its weight. According to Kerl-Stohmann's 'Chemistry,' vol. iv. p. 1458 (2nd ed.), a small still of that alloy at Halle, of 13 gals. capacity, with a daily output of 12 cwt. of vitriol, stood very well. Yet the iridium-platinum alloy has had to be given up, because it is too brittle; pure platinum, from its toughness, malleability, and capacity for welding, is more durable in the long run.

According to more recent statements by Scheurer-Kestner ('Comptes Rendus,' Nov. 1875) the losses of the platinum still at the Thann works were as follows:—during 2 years, a small quantity of nitrogen acids being present, 2·859 grms. for 1000 kilogs. strong vitriol of 93 or 94 per cent. SO_4H_2. In the following year, the nitrogen acids having been removed by ammonium sulphate, 1·220 grm. platinum for 1000 kilog. vitriol. In the following years, when the vitriol contained a little sulphurous acid, the loss of platinum fell to 0·925 grm. Small quantities of hydrochloric acid in the chamber make no difference in the solution of platinum. This, however, is done to a large extent when the strength of the vitriol exceeds the ordinary 66° Baumé (*so-called* 170° Tw., in reality only 1·83) of commerce, which contains at most 94 per cent. of SO_4H_2. The loss in making 180 tons of extra-concentrated vitriol with 97 to 98 per cent. of SO_4H_2 amounted to 6·07–6·65 grms. platinum per ton, in making 102 tons of vitriol of 99½ to 99¾ per cent. of SO_4H_2 even 8 to 9 grms.; by quantitative analysis 8·38 grms. platinum per ton were actually found.

The above-mentioned experiments only refer to the still itself; but even the accessories are subject to wear and tear, as is shown by the following Table :—

	Original weight.		Weight after 5 years' use.
Still..................	30·346	kilog.	26·450
Head	7·255	,,	7·000
Siphon	5·689	,,	5·520
Small parts.........	1·075	,,	1·000
	44·365	,,	39·970
	39·970		
Loss	4·395		

Since the still itself had only lost 3·896 kilog. of metal, there was a loss of 12·8 per cent. of the other parts.

This nearly agrees with the statements mentioned by Hasenclever (in Hofmann's 'Report,' 1875, i. p. 188), also originating from Scheurer-Kestner, according to which the loss with ordinary acid amounts to 1·92 grm., with acid containing SO_2 to 1·05 grm., for 1000 kilog.

According to Hasenclever's own experiments (*l. c.*) the loss of platinum at the Hantmont works only amounted to 0·252 grm. per ton of vitriol of 1·8 spec. grav.; if, however, the repairs and the loss in renewing the apparatus are taken into account, the expense amounts to 1·616 franc (=1*s.* 3*d.*) per ton of 1·8 sp. gr. At the Rhenania works the wear and tear of platinum amounts to 0·972 grm. of platinum, and the total expenditure for still-repairing to close upon 2*s.* per ton of 1·8 sp. gr. In both cases the acid was free from nitrogen compounds.

Quite recently (Compt. Rend. 29th April 1878) Scheurer-Kestner has made experiments on the waste of platinum in the preparation of fuming oil of vitriol. The latter was made by heating sodium pyrosulphate in an earthenware retort, lined inside with a sheet of platinum soldered by itself. This weighed 5 kilog.; and after preparing 100 kilog. fuming oil of vitriol it had lost 100 grms.—that is, 1 kilog. platinum per ton of acid. The platinum was found in a soluble form in the residual sulphate of soda. Scheurer-Kestner has moreover established the fact that with the modern platinum apparatus for making ordinary oil of vitriol, whether those of Faure and Kessler, or those of Desmoutis and Co., the quantity of platinum lost is only one fourth of what used to be lost in the former apparatus, viz. only 0·10 grm. per ton for ordinary 170° acid, and from 1·0 to 1·5 grm. per ton for acid of 98–99 per cent. He ascribes this, first, to the much lower boiling-point caused by the little depth of acid, and, secondly, to the much smaller weight of platinum; especially in Faure and Kessler's apparatus a much smaller platinum surface is in contact with the acid than formerly.

In Knocke's description of the Oker works (Dingl. Journ. cliv. p. 181) it is mentioned that formerly the platinum stills used to be fired with coals, but that wood had been introduced instead, because the still was found damaged in consequence of the sulphur contained in the coals. Even by the formation of carbon-platinum the platinum may become brittle; the fuel, therefore, ought never to come into immediate contact with it.

The *iron* salts contained in the chamber-acid in concentrating up to 170° Tw. are precipitated as *ferric sulphate*, which, being insoluble in strong vitriol, partly attaches itself in white crusts to the vessel, partly remains suspended in the acid in shining flakes; the precipitate also contains a little lead. When it occurs in large quantities (which, however, only takes place exceptionally, and probably never with pyrites in pieces) it may occasion stoppages of work and also make the acid more or less unsaleable. This especially happens when Glover-tower acid is employed for concentration. In order to remedy this, Gerstenhöfer suspended a large porcelain dish in the still by means of platinum wires, completely immersed in the acid, in which, owing to the boiling movement, all crusts &c. collect. It is therefore only necessary to take out the dish from time to time, which can be done very quickly (Bode, Beiträge, 1872, pp. 50, 51). This arrangement seems to have been introduced in very few places.

Other Methods for Concentrating Sulphuric Acid.

Such methods have been mentioned already in several places—for instance, Seckendorff's cast-iron retorts (p. 507), Clough's lead pans cooled by water (p. 492), Hemptinne's lead vacuum-pans (p. 513) and his apparatus with superheated steam (p. 511), and Stoddart's lead pan with a current of air (p. 506).

Roder (Dingl. Journ. cxi. p. 397) proposed enamelled cast-iron boilers, and indicated a special kind of enamel for them: 1 part of powdered burnt alum, 4 parts of red lead, and 2 parts of pure silica are to be melted together; the fluxed mass is to be cooled in water, dried, powdered, and 15 parts of it intimately mixed with 20 parts of pure silica and 3 parts of tin oxide. The whole is ground up with spirit of turpentine, laid with a soft-hair brush on the smoothly turned inner surface of the boiler; and this is repeated three or four times, each coat being allowed to dry first. The enamel is then fixed by fusing on as usual. Even the best enamel will certainly resist only a very short time the boiling vitriol and the uneven expansion and contraction of metal and enamel at the very greatly differing temperatures which occur here.

Gossage (Patent of 1850, Hofmann's 'Report of the Juries,' 1862, p. 17; Muspratt's 'Chemistry,' ii. p. 1047) allows the acid to meet a current of hot air in a chamber filled with pebbles. His apparatus consists of two parts (figs. 280 and 281), one of which serves for heating the air, the other for evaporation. The first object is effected by 16 iron tubes, *a a*, open at top and bottom, surrounded by the fire from *b*, which comes to them by the flue *c*. The flame travels downwards in the direction of the arrows, and escapes through *d* into the chimney. The cold air enters the tubes *a a* from below through an arch, *e*, and leaves them at *f*, strongly heated; it passes through *g* and *j* into the concentrating-apparatus. This consists of two concentric cylinders, *h h*, of ½-in. lead, leaving a space, *i i*, between them; at the bottom they are burnt to a lead plate. The inner cylinder is closed at the top, except in the centre, where it opens into the pipe *j*; its inner space is three-fourths filled with pebbles. When the iron tubes have been brought to a red heat, the acid to be concentrated is run onto the cover of the inner cylinder; it first fills the space between the two cylinders, and then flows through the tubes *k k*, loosely covered by dishes, into the inner cylinder, where it spreads over the pebbles. The hot air entering through *g j*, being in immediate contact with the vitriol, evaporates the latter quickly, and goes through L into the chimney, charged with steam [and acid vapour]. The acid becomes more and more concentrated as it gets lower down; and with a proper relation between the temperature of the air and the supply of acid, the latter can be drawn off, highly concentrated, by the pipe M. The space *i i* both serves for a preliminary heating of the vitriol and for protecting the lead cylinder. This apparatus has never come into use; its faults are the following:—The air must be made nearly red-hot; and thus the upper lead pipe always

Fig. 280.

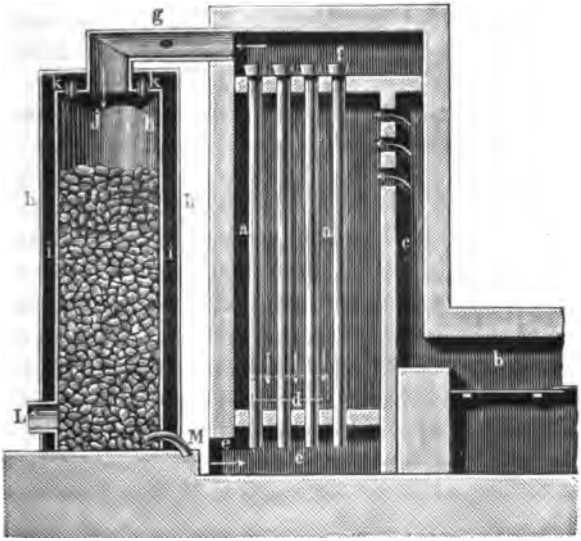
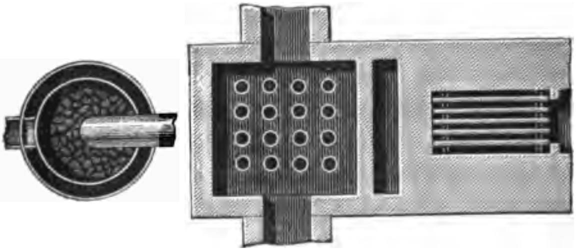


Fig. 281.



melts; the air, charged with vapour, travels in the same direction as the vitriol, and therefore again gives up its water to the latter as it becomes more highly concentrated; all acid escaping along with the hot air is lost in the chimney. Although some of these faults might be avoided by changing the details of construction, the apparatus seems never to have been employed in practical work.

Gossage's plan with heated air has been re-invented by Cotelle, without any additions (Chemical News, xx. p. 107).

Packages for Sulphuric Acid.

Sulphuric acid is mostly sent out in large glass bottles or *carboys* of about 15 gallons capacity, packed in baskets with straw, the projecting necks being still further protected by straw ropes. They are closed by earthenware stoppers dipped in melted brimstone and put in quickly before the sulphur has solidified. Mostly damp clay is put round the top, and a linen rag is tied all over it. Often, especially for short distances, the brimstone is omitted. The baskets only last a short time when exposed to the weather and the damp soil, and especially when any acid gets at them. This last is sometimes difficult to avoid; after once using, a few drops of acid run down the neck of the carboy and find their way to the bottom of the basket; and the floor of the warehouse, where they are placed, is not easily kept entirely free from acid. Therefore the bottom of the basket is damaged first; and on lifting the carboy the bottle filled with acid forces out the bottom of the basket by its weight and falls through. For this reason a damaged basket ought never to be sent out; some works go upon the principle of *always* packing the returned carboys in fresh baskets. The baskets stand much longer when they are dipped two thirds of their height in coal-tar. In England, baskets made of stout iron wire or of thin hoop iron are frequently met with, protected against quick rusting by a thick coating of coal-tar. In the north of England frequently, sometimes also in Germany, carboy-tubs are used, made of small staves, tapering a little downwards, and bound with iron hoops; the bottle is put in, packed in straw, with only its neck projecting; a circular cover, provided with a hole for the bottle-neck, is put on and fixed. These tub-carboys are rather clumsy and somewhat dearer than basket-carboys, but much more durable; and they afford the great advantage that railways, barges, &c. carry them in two tiers one above the other, which they never do with basket-carboys.

In America, cubical cases are employed, kept together by iron hoops; the bottles are put in with sea-weeds; they cost one third of a dollar per cwt. (Goldschmiedt, Austrian Report upon the Philad. Exhib. vii. p. 10). In France, and also at Aussig in Bohemia, stoneware jars of the size of ordinary glass carboys, and of the same clay as is used for "bombonnes" (acid-receivers), are frequently employed; these can be moved about at the works without baskets, but must be put into baskets for sending out. At Beauvais, where they are made, they cost 1½ franc each.

In spite of all precautions, it frequently happens that glass carboys get cracked, either in handling or by the jolting of railway-trucks; and the acid running out is not merely lost, but often does a great deal of damage. The railway and steamboat companies accordingly will only accept acids (vitriol, as well as other mineral acids sent in carboys) at the sender's risk, or else at very high rates for carriage, and only send them by certain trains. Under all circumstances, on account of the bulky nature of this merchandise, a very much higher rate is charged for its conveyance than corresponds to its weight. A truck which carries 10 tons of goods in casks can only carry about 2½ tons of vitriol in carboys. The additional cost of carriage is therefore in direct proportion to the accompanying dead weight and bulk; and as such the water must be regarded which is contained in acid of 144° Tw. (brown vitriol) over and above that in strong vitriol.

The cost of packages also amounts to a good deal. It differs very much, according as the situation is more or less convenient for purchasing the bottles &c.; but it will hardly ever be under £2 per ton of real acid, and is much higher for brown vitriol containing 78 per cent. of SO_4H_2 than for strong vitriol with 93 per cent. of SO_4H_2. To be sure, the empties are mostly returned; but there is always much breakage, and for longer distances the return-carriage is too dear.

It follows from this that it will only pay for a certain distance, differing very much according to local circumstances, to send out brown vitriol of 144°–152° Tw.; when the distance exceeds that limit, the extra cost of packages and transit becomes equal to or more than the cost of extra concentration, and the consumers prefer to buy strong vitriol of 170° Tw. It cannot be denied that frequently old habit or, more strictly speaking, ignorance causes consumers to buy acid of 170° when acid of 144° would be cheaper for them. On the other hand, of late years acid of 144° has been sent very much longer distances than formerly by means of *canal-boats* lined with lead, or *lead cylinders* mounted on railway trucks, instead of carboys. Evidently this can only be done in the case of buyers who can not only take a whole boatload or truckload at a time, but also empty it at once in order to return the vessels. The Oker works send out most of their chamber-acid and brown vitriol in lead cylinders holding 7½ tons, but the strong vitriol in glass carboys.

Balmain and Menzies have taken out a patent for conveying vitriol safely and cheaply in *iron vessels*, provided that it is not below 130° Tw., that the outer air is excluded, and that the vitriol contains no impurities acting on the iron. In America, indeed, concentrated sulphuric acid and even nitric acid are supplied to the nitroglycerine-makers in the same large sheet-iron drums in which the glycerine has been imported from France (Goldschmiedt, *l. c.* p. 10).

On the Rhine, copper cylinders are generally used for this purpose, sometimes also sheet-iron cylinders, with the precautions mentioned by Balmain and Menzies; there, however, 144° Tw. is the lowest limit of strength.

CHAPTER XIV.

ARRANGEMENT OF THE APPARATUS OF SULPHURIC-ACID WORKS.

ALTHOUGH it is obvious that no general rules can be laid down for this, perhaps a few remarks upon it will not be out of place. Of course the arrangement of acid-works depends, first, upon whether they are only to supply chamber-acid or strong acid. In the latter case, if no Glover tower or no pans on the pyrites-burners are present, space is needed for concentrating to 144° Tw., and at all events for the last concentration of the acid. If this is effected in glass retorts, there must be in any case a special house provided for this purpose, with a tight roof, double doors, &c., as previously described. The platinum apparatus, however, according to any of the systems described in the last chapter, can be placed anywhere, as they take very little room. If the chambers placed are high enough, there is no reason why all the concentrating-apparatus, even the glass-retort house, should not be put underneath them, although the same space will not be available for storage of ore, acid-carboys, &c.; but no general rules can possibly be laid down for this.

Without taking any further notice of the last concentration of the sulphuric acid, we remark as follows on the arrangement of the remaining apparatus. The lowest level is always occupied by the pyrites- (or brimstone-) burners; only there must be space left for wheeling away the cinders. Accordingly the burners are always erected on the ground-level; and the stone-breakers, if present, are mostly found on the same level. The pyrites in large works arrives on a railway resting on trestles (gears) and is tipped between the trestles, in order to be taken away as it is wanted, to be broken and laid in front of the kilns. Where the supply of ore is quite regular, the stone-breaker can be disposed so that the ore will pass direct from the railway-trucks through the breaker, and arrive broken on the ground-level, thus saving labour. Where the ore is broken by hand, or where it arrives in large and irregular parcels, this cannot be done very well.

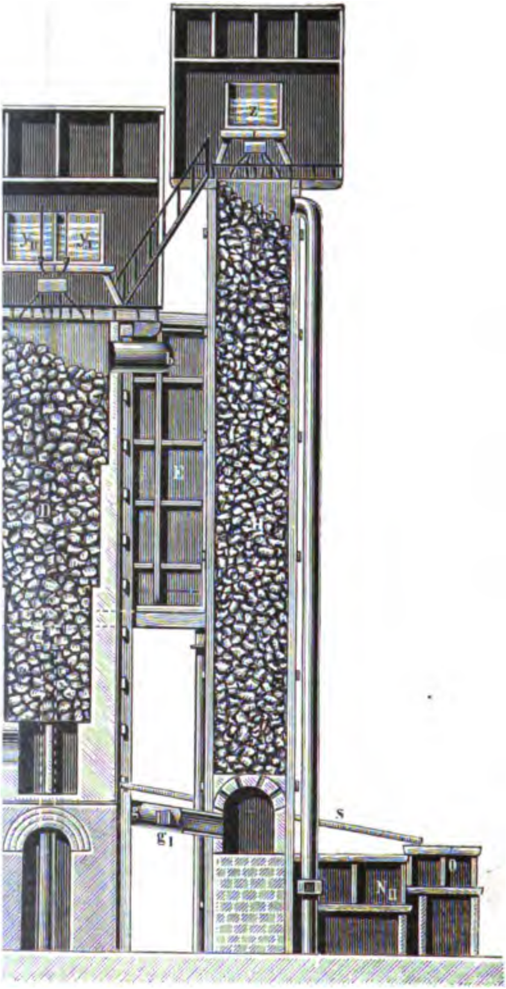
Unbroken pyrites, especially non-cupreous, can be stored in the open air without much damage; but after breaking it ought to be protected from the rain. It is sifted directly after; the dust is stored apart from the lumps; and both are taken to the burners across a weighing-machine. The breaking, sifting, and storing of the broken pyrites nearly always takes place underneath the chambers. Where these are high enough above the ground, the burners themselves are also placed beneath them; otherwise they are erected in a separate shed immediately adjoining. Any cooling-pipes or tunnels are arranged along the side or on the top of the chambers. Where the burners are built under the chambers, the outer pillars of these must be connected by a light wall, to keep the wind off the burners.

The nitre-ovens are nearly always built at the end of each set of burners and as a continuation of it.

The steam-boiler is also sometimes placed under the chambers; it is better to put it in a shed outside, both in order not to injure the timber of the chamber-bottom by steam leaking or blowing out of the safety valves, and to save the boiler plate from being corroded by any accidental droppings of acid. In case of an explosion the damage will then not be quite so serious as if the boiler stood directly under the chambers.

As the burners are built on the ground-level, as the chambers are in any case erected at a certain height above it, and as the gas-pipe also enters into the upper part of the chamber, the gas-pipe must necessarily rise a good deal; and the conditions of draught are thus satisfied.

If, however, a Glover tower is to be used, it must be placed between the burners and the chambers. Sometimes a few burners are set aside for working the nitre-ovens by their heat and taking the nitre-gas direct into the first chambers; generally this is not done, but each set of burners is followed by the nitre-ovens and then by the Glover tower. Where liquid nitric acid is employed, the nitre-oven is simply left out. The Glover tower itself must be


Z
YII
YI
E
D
H
g1
S
NII
O

placed with its base rather higher than the top of the gas-channel over the burners, so that the gas need not descend in order to enter the tower. It is also desirable that the gas issuing from the tower should be led to the chamber through a horizontal or, still better, slightly ascending pipe. From this it follows that the base of the chambers themselves must be sufficiently elevated to allow this. If, for instance, the top of the Glover tower (apart from the acid-tanks) is 36 feet above the ground, and the chambers themselves are 20 feet high, the latter ought to be founded on pillars at least 20 feet high, so that the gas-pipe coming from the tower can still enter the chamber below the top of the chamber. If this cannot be done (if, for instance, a Glover tower has to be put to a set of chambers already built), the gas must be taken downwards, which will involve a somewhat complicated construction of the chamber-top joists, by no means contributing to their stability. On the other hand, the chambers are sometimes placed so high that the top of the Glover tower is below their bottom, and the chamber-acid can be run directly into the tower. This is done at a few English and at the Oker works.

The chambers, as mentioned before, are either arranged so that their floors are all at the same level, or so that each following chamber is from 1 to 3 inches higher than the preceding one. A greater difference is not necessary, but is sometimes found for local reasons. From the last chamber issues a pipe connecting it with the Gay-Lussac tower, which can only exceptionally be placed on a foundation so elevated that this pipe need not descend—certainly a preferable arrangement if the levels permit it. Provision must also be made for interposing a long cooling-channel between the last chamber and the Gay-Lussac tower.

In any case the Gay-Lussac and Glover towers ought to be combined into a set, with the necessary tanks, air-pump, acid-eggs, &c. arranged at the foot, by which the attendance will be much facilitated. In large works with several sets of chambers it is preferred rather to combine several Glover towers, and in any case several Gay-Lussac towers, to form a set.

Although it is of course impossible to lay down a universal plan for building sulphuric-acid works, a generally suitable arrangement is shown in figs. 282 & 283.

Here no account is taken of the concentration up to 170° Tw. If done in platinum, it takes very little space, and room is easily found for it. Further, in order to make the diagram clearer, the pyrites-burners are not assumed to be placed underneath the chambers; that place will be easily utilized for storing pyrites, coals, carboys, &c., or else, if it is to be used for the kilns or other apparatus, the arrangement can easily be modified to suit this. As the plan is only meant for a block plan, only the essential parts are indicated: in particular, the chambers are only sketched in section; the other apparatus are shown as viewed from above. The sectional elevation, fig. 283, follows the lines P Q R S T U of the plan.

The whole begins with the pyrites-burners, A A B B, of which 16 are present, in two rows built back to back. It will be preferable to move these burners, represented here as contained in a shed of their own, further away from the chambers than they are drawn here, in order to get 10 feet or, better, 13 feet of space for charging. If the burners are underneath the chambers, there will anyhow be room for this. We assume here that 12 of the burners (A A) send their gas directly into the Glover tower, and 4 of them (B B) into the nitre-oven C, in which there are two semicylinders for receiving the mixture of nitrate and vitriol. If liquid nitric acid is used, there is no nitre-oven, and the burners all communicate directly with the Glover tower, in which the nitric acid is run down along with the other acids. The cast-iron pipe *a* takes the gas from A A to the Glover tower, and the lead pipe *b* from this to the chamber. From the nitre-oven the gas first ascends in a vertical metal pipe *c* in order to be cooled and to enter the chamber through the elbow-pipe *c'*. The currents of gas from *b* and *c* cannot check each other, as they enter in the same direction, and as the steam-jet *i* enters between them. Still the arrangement as drawn is not without fault: the metal pipe *c* from C must be continued into a lead pipe *c'*, which is easily damaged by overheating, especially at the joint between metal and lead; and, on the other hand, if the pipe is cooled, sulphuric and nitric acids are condensed to the liquid state, flow down the metal pipe and destroy it. For this reason most works do *not* proceed as shown in the diagram, but allow the gas from *all* the pyrites-burners to pass through the nitre-oven and then into the Glover tower. The fear at first entertained that the nitre-gas might be partially destroyed in the tower has been long since refuted by experience.

From the first chamber, E, the gas travels through *d* into the second chamber, F, and thence through *e* into the last chamber, G;

from this through the pipe *f* and its long continuation *g*, into the Gay-Lussac tower, H. The latter stands alongside the Glover tower; both have a common platform at the top; and close to them are the tanks, acid-eggs, &c. The great length of the pipe *g* is desirable simply for cooling the gas before it enters the Gay-Lussac tower. *g'* is a "sight" for observing the colour of the gas.

The three chambers are drawn as 100 ft. × 20 ft.; and if they are taken as 20 ft. high, their cubic contents will amount to 120,000 cubic feet. In the 16 burners 5½ tons daily of 48-per-cent. pyrites can be burnt, which represents rather more than 20 cubic feet of chamber-space for each pound of sulphur contained in the pyrites *charged* (not burnt). This is fully sufficient; and even 10 per cent. more pyrites might be burnt without doing any harm whatever. The Glover tower is 8 ft. 10 in. × 8 ft. 10 in. × 30 ft., the Gay-Lussac tower 6 ft. in diameter and 45 ft. high. The steam is furnished by two boilers I and K, of which I works with low-pressure, K with high-pressure steam; instead of the latter, of course, a pipe may be taken to the chambers from the principal steam-boilers of the factory, if there are more boilers there. The low-pressure steam from I travels through the pipes *h h*, and at *i*, *k*, and *l* (fig. 282) sends jets into the three chambers, always in the direction of the draught; just for this reason it is not too quickly condensed and supplies also the opposite chamber-end, either in the state of vapour or of mist. The high-pressure steam from K only supplies the air-pump, L, through *m*; the exhaust-steam from the steam-cylinder enters, through *n* and the stop-valve *o*, the low-pressure main, *h h*, and is utilized there. In order to be able to use the steam from K directly for the chambers in case of I being under repair, there is a communication-pipe with a usually closed valve, *p*.

The pumping of the acids is done in the following way. From the Gay-Lussac tower, H, the nitrous vitriol runs into the lead-lined tank N_{IV} through the lead pipe *t* or through an open lead spout, which is not so easily stopped up. The strong acid from the Glover tower runs through the open spout *s* into the tubular cooler O (comp. p. 405), or simply through a small tank provided with a lead worm for cold water (p. 406), and from the other end enters the dividing-box *u*, so that it can be let run into either the tank N_I or N_{II}. The former serves for storing the acid required for working the Gay-Lussac tower, which must be especially strong and well cooled; it is raised to the necessary height by means of the pressure-valve r (p. 396), the acid-egg M (p. 395), and the delivery-pipe w, and arrives in the cistern z on the top of the tower H. The strong acid intended for sale or use is run into the tank N_{II}; it generally need not be quite as strong nor (for use) cooled, and can be diluted in N_{II} with chamber-acid which arrives from the first chamber through the pipe v. Usually, however, the latter goes to the tank N_{III}, from which it is raised to the top of the Glover tower by means of the valve $r_{,}$, the acid-egg M_I, and the pipe x; there it is kept in one of the two cisterns y_I or y_{II}, the other of these getting nitrous acid from N_{IV}, which is pumped up by the same apparatus. The pipe q, coming from the air-pump, conducts compressed air alternately into the two acid-eggs, one of these always working whilst the other one is getting filled. The arrangement as drawn, with two acid-eggs, four tanks of 10 × 10 × 7 feet, and a tubular cooler of the size shown, is quite sufficient for two sets of chambers; the second set might be symmetrically joined to the first, so that the Gay-Lussac and Glover towers, standing in a line with H and D, could be served from the same platform. Also the steam-boilers, if large enough, would suffice for both sets. In large works it is preferred to have all the chambers in a continuous row without any gap between them; this is attained by placing the apparatus L, M, N, O underneath the chambers, which is easily done, as they have no great height. Then, of course, the steam-boilers I and K must either be also placed underneath the chambers, or erected a little further out. In the design here represented the idea is that *one* man attends to the firing of the boilers, to the air-pump, L, and to all the pumping-apparatus and cisterns, which is easily done, especially if the boilers are fired from the side nearest to the pump L. If it is also preferred to build all the pyrites-kilns A B in a row, they can be placed on the side of the towers opposite to the chambers; the gas would then enter the Glover tower at α and leave it at β, which would provide a very straight path for it. This arrangement will come of itself if, as mentioned above, the burners be placed about 7 feet further away from the chambers, in order to gain more working-space for them.

CHAPTER XV.

YIELDS AND COSTS OF SULPHURIC-ACID MANUFACTURE.

In calculating the cost of manufacturing sulphuric acid, we must take into account the following factors:—

Cost of raw material (brimstone or pyrites);
Consumption of nitrate;
Consumption of fuel;
Wages;
Wear and tear of apparatus;
Interest on capital, general expenses, &c.;
Yield of sulphuric acid.

The last is the most decisive factor; for the others (excepting the consumption of nitre) only to a small extent depend on the carefulness of the manufacturer, the suitability of the apparatus, &c. We will therefore in the first place inquire into the *consumption of nitre* and the *yield*. We are here met at the outset by the difficulty of comparing the statements from different sources, arising from different fundamental quantities being taken as the basis of the calculation. Some calculate all the sulphur contained in the charge, others only that portion which has actually been burnt, not taking into account the sulphur left in the cinders. The latter way of calculating is more rational in theory; but in practice it is less useful than the former. For it is known with perfect accuracy how much pyrites and how much sulphur contained in it has been put into the burners; but as the percentage of sulphur in the cinders varies, it is not known precisely how much has been burnt. Besides the question is not only how the chamber process itself works, but also how the burning has been done, on which the smaller or larger residue of sulphur in the cinders depends.

In the following we shall reduce all statements, so far as it can be done from the sources, to *sulphur contained in the charge*. The *consumption of nitre* is stated sometimes in percentages of pure sodium nitrate, sometimes in percentages of commercial nitrate; and in the latter case either 95, 96, or 97 per cent. is assumed. Here also we have a source of uncertainty and divergence, although not of such importance as that just mentioned. To each part of sodium nitrate correspond 63·53 parts of N_2O_5 or 74·12 parts of NO_3H or 134·76 of nitric acid of 1·34 sp. gr. (at 15° C.), the strength usually employed in vitriol-works.

The worst confusion prevails regarding the calculation of the *yield of sulphuric acid.* Some state it in terms of chamber-acid of 50° Baumé (=106° Tw.), some as 60° Baumé (=144° Tw.), some as commercial 170° Tw. (=66° Baumé), some as real monohydrate; what is worse, the reduction upon these terms is made by very varying and, in part, quite erroneous tables (comp. p. 28); and frequently it is quite uncertain whether by "oil of vitriol" (O. V.) or "acid of 170° Tw." an acid of 93 to 94, or one of 96 to 98, or one of 100 per cent. SO_4H_2 is meant. In the following, so far as the sources permit, all statements will be reduced to the only rational term, that of monohydrate, SO_4H_2.

Frequently, at works where none of the sulphuric acid is sold, but the whole is used for making salt-cake, the yield is calculated indirectly, from the quantity of common salt decomposed by it, according to more or less arbitrary assumptions regarding the quantity of sulphuric acid consumed for decomposing a unit of salt. Thus several large manufacturers, working with open roasters, assume a consumption (and consequently a make) of 81·33 parts of SO_4H_2 to each 100 parts of common salt. Now in muffle furnaces (blind roasters) decidedly less vitriol is consumed than in open roasters; and yet a large Alsatian maker, using blind roasters only, assumes a consumption of 74 per cent. of vitriol of 66° Baumé on the sulphate, =85·8 per cent. on the salt, or 80·8 per cent. of real SO_4H_2 on the salt, which is all but equal to the above-named figure. This proves the uncertainty of such bases of calculation.

Consistently, several English works have latterly given up calculating the yield of sulphuric acid altogether; they only state the yield of salt-cake upon the pyrites burnt, or upon the sulphur contained therein.

Often no mention is made whether that portion of the sulphuric acid employed for the *decomposition of nitre,* which leaves the factory in the shape of acid sulphate, has been allowed for in the calculation. We do this in the following, wherever it can be done from the sources.

Of course the following enumeration does not contain all and every statement of the kind scattered in innumerable publications, but only so much as suffices for forming a good idea of the state of matters.

I. CONSUMPTION OF NITRE.

1. *For Brimstone Acid.*

(a) *Without Recovery of the Nitre-gas.*

To 100 parts of brimstone charged:—6 to 9 parts (Knapp, Chem. Technologie, 1866, i. pp. 2, 298); at least 6, sometimes 7½ parts (Schwarzenberg, *l. c.* p. 400); 6 to 8 parts (Payen, Précis, 1877, i. p. 322); 7 to 8 parts (Scheurer-Kestner, in Wurtz's Dict. de Chim. iii. p. 158); 8·9 parts (Stevenson and Williamson, in Richardson and Watts's Chem. Technol. iii. p. 318); 10 parts (Wright, Chem. News, xvi. p. 93).

(b) *Recovering the Nitre-gas.*

4 to 5 parts (Knapp, *l. c.*); 3 parts (Schwarzenberg, *l. c.* p. 401); 5 parts (Payen, p. 322); 3 to 4 parts (Scheurer-Kestner, *l. c.*).

2. *For Pyrites-acid.*

(a) *Without Recovery of Nitre.*

At the Oker works in 1857, 14·4 parts; 1859 to 1863, 13·4 to 300 parts strong vitriol (Knapp, Kerl-Stohmann); to 100 sulphur charged in the shape of pyrites, 10 parts (Schwarzenberg, *l. c.* p. 432), 9 to 11 parts (Payen), 12 to 14 parts (Scheurer-Kestner). According to Wright (*l. c.*), in different works, with pyrites of 45 to 50 per cent. 8·5 parts, of 30 to 50 per cent. 10 to 12 parts, of 35 per cent. 12·5 parts; with a set of chambers in bad repair, in the first year 9·31, in the second 9·84, in the third 10·02 parts. According to Gossage (*ap.* Richardson and Watts, p. 317) 13·3 parts with 30 per cent. Irish pyrites. From the author's own experience, on an average, with pyrites of 40 to 44 per cent. 10·8 parts; in neighbouring works 10·5 parts with smalls, 9·4 with lumps. At some French works the author was informed of a consumption of 1·5 to 1·97 kilog. nitre per 100 kilog. acid of 50° Baumé, equivalent to 2·9 to 3·8 kilog. per 100 kilog. pyrites of 44·4 per cent., or 6·5 to 8·5 kilog. per 100 kilog. of the sulphur contained therein. [This statement appears not trustworthy, viz. too low, looking at the figures from the same source for working with a Gay-Lussac tower.]

(b) *Recovering the Nitre-gas.*

To 100 sulphur in the pyrites:—5 parts (Schwarzenberg, p. 432); 7 parts (Payen, p. 322); 7 to 8 parts, less with higher towers (Scheurer-Kestner, *l. c.*); 3·8 parts (Glover). According to the author's own experience (with insufficient absorbing-space) 3·5 to 4·5 parts; but when the work was irregular, chambers out of repair, as much as 6 or even 7 parts. Neighbouring large works 3·5 parts. K. Walter guarantees 0·7 part of nitre to 100 parts acid of 66° Baumé=2·04 parts to 100 sulphur in 44-per-cent. pyrites. At the Oker works (Bräuning) 3·75 to 4·5 parts per 100 sulphur were used with pyrites pretty rich in sulphur, 4·5 to 6 parts with mixed and galeniferous ores. In French works (same source as above), per 100 kilog. acid of 50° Baumé 0·9 to 1·24 kilog., per 100 pyrites 1·73· to 2·38, per 100 sulphur charged 3·85 to 5·37 parts of nitre. According to notes collected by the author in 1878:—in German works, 2·3 to 3·1 nitre per 100 sulphur; in the best English works, about 3 per cent. (exceptionally, as stated by Affleck, 2·2 per cent.; in Lancashire many large works use even 5 per cent.); in French works, (with a Glover tower) 2·7 parts, (without) 4·2 to 4·7 parts to 100 sulphur charged.

In winter there is always less nitre used than in summer. As between nitric acid and solid nitre no difference worth mentioning can be established; if any thing, slightly less nitre is used in the solid form than as nitric acid, if not the acid itself, but the nitre from which it was originally made, be calculated, as it ought to be.

Hjelt (Dingl. Journ. ccxxvi. p. 174) has drawn attention to a circumstance overlooked up to that time, from which the difference in the consumption of nitre in works otherwise managed in the same way can be, at least partially, explained. According to him, the arsenic in chamber-acid is mostly in the state of As_2O_3, but on passing through the Gay-Lussac tower it is partly oxidized to As_2O_5, so that in a special instance the Glover-tower acid contained only 0·041, the Gay-Lussac acid 0·132 per cent. As as As_2O_5. Since the As_2O_3 is oxidized at the expense of nitrous acid, according to the equation $As_2O_3+2N_2O_3=As_2O_5+4NO$, in that case 0·096 N_2O_3, equal to 0·159 NO_3H, must have been destroyed for each 100 parts of SO_4H_2 passing through the tower. If only half of the whole make of acid passes through the tower, the loss of nitric acid of 36° Baumé caused by the arsenic amounts to 0·18 per cent. of the total SO_4H_2 made. The whole consumption in that special case was 1·62 nitric acid to 100 parts of oil of vitriol (=3·6 parts of nitre to 100 sulphur burnt), of which the above 0·18 part is a fraction not altogether to be neglected. In support of his view that the consumption of nitre to a certain extent depends upon the arsenic contained in the pyrites, Hjelt makes the following statements on the consumption of nitric acid at 36° Baumé upon 100 parts of pure SO_4H_2 made. The works alluded to above consumed with Westphalian pyrites containing 0·30 per cent. As (furnishing an acid with 0·014 per cent. As) only 1·32 part nitric acid, as against 1·62 part when Spanish pyrites containing 0·91 per cent. As was used. At Freiberg, where the acid contains 0·05 to 0·30 per cent. of As, 1·7 per cent. of nitric acid is used. At Grevenbrück, with Westphalian pyrites, 1·10 part; at Stolberg, with the same pyrites, 1 part; at Beuel near Bonn, with pyrites containing 1 to 1·5 per cent. As, 1·5 to 2 parts. Hjelt's own synopsis shows that the differences in the consumption of different works *burning pyrites of equal percentage of As* amount to several times the total loss which the arsenic could possibly have caused; accordingly this matter cannot have quite the importance which he attributes to it. According to his figures the maximum loss of nitre with pyrites containing more arsenic than any other could only amount to 0·12 part of nitre per 100 parts of oil of vitriol made.

Davis (Chem. News, xxxvii. p. 155) certainly comes to another conclusion, viz. that the largest portion of all the nitre lost in sulphuric-acid-making is spent in oxidizing the arsenious acid in the absorbing-towers, and that this loss can be proved directly as nitric oxide in the escaping gas. Thus Davis claims to have traced 82 to 87 per cent. of the total loss of nitre to the arsenic. But this conclusion is not justified; for, in the first place, he assumes that the whole of the As_2O_3 in the absorbing-tower is oxidized to As_2O_5, which, according to Hjelt (and several analyses by the author) is certainly not the case; secondly, his calculations all depend upon anemometrical measurements, the untrustworthiness of which is well known; and, thirdly, he proves too much, since he makes it incomprehensible whence the loss of nitre comes in making brimstone-acid, where arsenic is absent. Davis subsequently (*ib.* p. 195) ceases to maintain his former conclusions with any thing like certainty.

II. Yield of Sulphuric Acid (SO_4H_2).

(Theoretically 306·25 parts per 100 sulphur.)

1st. *From brimstone* (always upon the sulphur actually burnt). 290 to 300, on the average 296 (Knapp); 297 SO_4H_2=319·35 acid of 66° Baumé (Schwarzenberg); "usually 296 to 300; even the theoretical quantity has been obtained" (sic! Payen, i. p. 321); 290 to 300 (Scheurer-Kestner).

2nd. *From pyrites.* At Oker, in 1857, 1 cwt. acid of 66° Baumé per 1·89 cwt. ore (Knapp); 1859–63, per 1·729 cwt. ore (Kerl-Stohmann); 1877, in the same place, 160 chamber-acid of 50° Baumé (106° Tw.) were obtained from 100 pyrites; from 100 rich copper-ores 140 to 150 parts of chamber-acid, from 100 "mixed ores" 90, from 100 ore mixed with galena 70 parts of chamber-acid. The residual sulphur in the cinders from pyrites (always containing galena) amounts to 6 per cent., from the other ores to 10–12 per cent. (Bräuning).

In four Belgian works, 1854 (Official Report), on 100 parts sulphur in the pyrites charged 242, 237, 259, 238 parts SO_4H_2. The same works in 1874 by improved arrangement had arrived at 87·81, 92·17, 85·50, 89·30 per cent. of the theoretical quantity, or 268·8, 282·4, 261·8, 273·5 SO_4H_2 per 100 S (Chandelon).

In the *best* French works (Schwarzenberg), on 100 sulphur in the pyrites charged, 259·7 SO_4H_2; on the sulphur really burnt, 283·43. Payen (p. 322) makes precisely the same statement, with the addition that *usually* from 100 kilog. 46-per-cent. pyrites 100 to 115 kilog. acid are obtained (=239·1 to 250 SO_4H_2 per 100 sulphur). According to Scheurer-Kestner (*l. c.*) there ought to be the same yield on the really burnt sulphur of pyrites as upon brimstone, viz. 290 to 300 parts (?). According to Wright, with rich

Spanish pyrites 82 to 84 per cent. of the sulphur is obtained as acid; of the loss of 16 to 18 per cent. 4 or 5 per cent. is sulphur left in the cinders, and 12 or 13 per cent. other losses. This means a yield of 251 to 257·25 SO_4H_2 per 100 sulphur charged (evidently with insufficient chamber-space). An anonymous chemist (in the Chem. News. xiv. p. 22) states the yield from 30-per-cent. Irish pyrites = 82 to 81·1 per cent. of the theoretical, inclusive of the sulphur in the cinders.

The author's own experience, and reliable statements personally obtained by him from large factories (where, however, the acid made was mostly calculated from the salt decomposed), are as follows:—(*a*) 238·5 SO_4H_2 on the sulphur charged, with 40-per-cent. small pyrites burnt in muffle furnaces; (*b*) 240 SO_4H_2, ditto, with 42-per-cent. lump ore: both without a Gay-Lussac tower. (*c*) 263·2 on sulphur charged (own experience), with Gay-Lussac tower, but the work being several times interrupted. (*d*) 272 to 275 ditto (own experience), with a Glover and a Gay-Lussac tower, the latter not large enough. (*e*) 276·4 on the sulphur charged, or 301·5 on the sulphur burnt (average result of a large, well-managed factory with Glover and Gay-Lussac towers). (*f*) a number of notes collected in 1878 from the best German and French works agree remarkably closely to a yield of 270–272 SO_4H_2 on the sulphur charged. In the warmer climates the yield, even with sufficient chamber-space, is always found somewhat less in summer than in winter, about 3 per cent.

Losses in Manufacturing Sulphuric Acid.

The causes of the *loss of nitre* have been mentioned in detail, p. 453. They are (1) loss of nitre-gas carried into the outer air, (2) nitrogen compounds left in the chamber-acid, (3) nitre-gas reduced to N_2O or N.

The *loss of sulphuric acid itself*, amounting even in the best works to at least 12 per cent. of the sulphur charged, arises from the following causes:—

1. Incomplete combustion of the sulphur (loss in the cinders); this has also been spoken of before (p. 173). With brimstone this loss is not worth mentioning; with pyrites it is so much the greater the poorer the ores are, and besides it varies enormously according to the construction of the burners and the care with which they

are worked, from 1 to 10 parts and more of sulphur per 100 pyrites, or from 2 to 30 per cent. of the total sulphur. A portion of the sulphur is sublimated, and is found in the connexion-pipes and in the acid itself, and is a clear loss.

2. Losses of SO_2 by leakages of burners, pipes, chambers, &c. By bad draught much loss may occur, since at the doors of the burners, nitre-ovens, &c. it continually blows outward. Bad pipe-joints, but especially chambers worn down too much, lead to great losses. The author has seen chambers which, when ultimately stopped, presented in their interior the image of the starry sky from the innumerable holes in the top; and Wright (Chem. News, xvi. p. 93) has independently used the same simile. Many manufacturers have no idea of the great loss which they suffer in this way, by allowing, from motives of ill-timed economy, a chamber to go on too long and trying to patch it up. Wright found in a chamber system that went three years without repairs:—

	Nitre for 100 parts of sulphur burnt.	Cubic metres of chamber-space per kilog. of sulphur burnt per diem.	Practical yield (theoretical =100).
First year	9·31	1·150	81·5
Second year ...	9·84	1·073	75·4
Third year	10·02	1·017	68·4

3. Losses of SO_2 by *incomplete conversion into sulphuric acid.* Extremely little SO_2 can remain dissolved in chamber-acid if there is an excess of nitrous compounds present; the greater portion of any remaining SO_2 escapes from the chambers into the outer air. The reason of this may be irregularity of the process in general, want of nitre, insufficient chamber-space, insufficient draught, &c., as explained in detail previously. The losses from this source are nearly always much greater where the nitre is not recovered, for the reasons stated above. The very widely divergent statements on the yield of sulphuric acid are explained to a great extent from this cause alone.

Mactear ('Chem. News,' xxxvi. p. 49) has asserted that a rational chamber-process cannot possibly be carried on without the constant testing for the loss of sulphurous acid introduced by himself. But it is very certain indeed that the factories thus controlled do not obtain any better yield of sulphate than other well-managed works.

Some contend that they have greatly lessened their losses by that control; but that only proves their former management to have been faulty.

The consumption of coals for chamber-steam only amounts to 16·3 kilog. per 100 kilog. SO_4H_2 on the average of eight French factories working without Glover towers; at an English works with Glover tower the coal used for the chambers and the air-pump amounted to 17·5 parts per 100 parts of SO_4H_2.

Statements of Costs for the Manufacture of Sulphuric Acid.

1. From brimstone.

At Marseilles, 1867 (Kerl-Stohmann, iv. p. 1495).

		francs.
1000 kilogs.	brimstone	170·00
75 „	nitrate of soda, @ 40 francs	30·00
100 „	coals	2·50
Wages		4·00
General expenses		6·50
		213·00

Yield 4000 kilogs. acid of 53° B. (=115° Tw.), which thus cost 5·32 francs per 100 kilogs.

2. From pyrites.

In Belgium, 1877, according to Lacroix (Kerl-Stohmann).

		francs.
1000 kilogs.	pyrites, @ 35 per cent. sulphur	35·00
42 „	nitrate of soda, @ 38 francs	15·96
150 „	coals, @ 1·20 franc	1·80
Wages		3·00
General expenses, repairs, &c.		3·00
		58·76

Yield 1365 kilogs. acid of 53° B.=4·30 francs per 100 kilogs.

In France, 1876, according to Favre ('Moniteur Scientif.' 1876, p. 273).

	francs.
640 kilogs. pyrites of 35 to 40 per cent. S., @ 30 francs	19·20
18 ,, nitrate of soda, @ 38 francs	6·84
30 ,, acid of 144° Tw. for decomposing the nitrate, @ 30 francs	1·20
80 ,, coals, @ 30 francs	2·40
Stone-breaking and other manual labour	3·26
Repairs and general expenses	5·00
	37·90
Deduct 20 kilogs. nitre-cake, @ 5 frs.	1·00
Cost of 1000 kilogs. sulphuric acid of 50° B. (=106° Tw.)	36·90

(The strength is calculated from Vauquelin's tables, and corresponds to 66 per cent. of SO_4H_2.)

In England the author himself found (at his own or neighbouring works) the cost per ton of SO_4H_2:—

a. From 40-per-cent. Belgian small pyrites burnt in a muffle furnace.

	£	*s.*	*d.*
1·048 ton pyrites, @ 18*s.* 8*d.*	0	17	5·600
0·044 ,, nitre, @ £15	0	6	7·200
0·557 ,, coals, @ 4*s.* 6*d.*	0	2	6·079
Sundry tools, materials for repairs, &c.	0	3	5·586
Wages: *a.* regular	0	6	2·186
,, *b.* extraordinary (repairs &c.)	0	1	7·044
	1	17	9·695
Deduct value of acid nitre-cake	0	1	1·200
Cost of oil of vitriol per ton	1	16	8·495

b. From Norwegian and Westphalian lump ore (without Gay-Lussac tower).

	£	*s.*	*d.*
0·9795 ton of pyrites (containing 0·4165 ton of sulphur), @ 23*s*. 6½*d*.	1	3	0
0·0393 „ nitre, @ £16	0	12	7
0·1250 „ coals, @ 4*s*.	0	0	6
Wages	0	7	5
Materials, repairs, &c.	0	2	0
	2	5	6
Deduct value of nitre-cake	0	1	6
Cost of oil of vitriol per ton	2	4	0

c. From cupreous Norwegian pyrites, with Gay-Lussac and Glover tower, in 1873:—

	£	*s.*	*d.*
0·838 ton of pyrites (with 0·38 ton of sulphur), @ 25*s*. 6*d*.	1	1	4·428
0·0172 „ nitre, @ £12	0	4	1·536
0·171 „ coals, @ 10*s*.	0	1	8·520
Wages for the process itself	0	6	9·520
Repairs (including wages)	0	0	10·464
Renewal of chambers (spread over the acid)		1	0
Cost per ton of oil of vitriol	1	15	10·468

(N.B. The coals did not include those used for pumping the acid.)

d. From cupreous Spanish pyrites, in 1876:—

	£	*s.*	*d.*
0·758 ton of pyrites (with 0·364 ton of sulphur), @ 19*s*.	0	14	4·80
0·0145 „ nitre, @ £11	0	3	2·28
0·250 „ coals, @ 4*s*.	0	1	0·00
Wages for the process	0	3	6·00
Repairs	0	0	6·00
Renewal of chambers	0	1	0·00
	1	3	7·08

In all these cases the acid obtained is of 140° to 144° Tw.; the cost of concentrating it further has been mentioned previously (p. 525).

CHAPTER XVI.

BY-PRODUCTS OF THE MANUFACTURE OF SULPHURIC ACID.

The most important of these in the case of cupreous pyrites is the copper itself, along with the iron oxide (obtained in this case in a sufficiently pure form), sometimes also with silver; we shall go into this in detail afterwards. From non-cupreous pyrites, however, iron and zinc are only exceptionally obtained. We do not, of course, refer to metals whose production is the principal object of the whole process.

Besides, thallium and selenium may be mentioned as by-products of sulphuric-acid making.

The cinders from non-cupreous pyrites (as to their composition comp. p. 175) are frequently used *as ballast for making roads*; they yield very firm, dry, and even roads, which, however, are soon ground into dust by the traffic of vehicles, and in wet weather are then very muddy. Besides, the rain-water washes out iron and zinc sulphates, and may carry these into neighbouring wells (Sarrazin, 'Archiv der Pharmacie,' ccix. p. 418).

These cinders have frequently been proposed for the *absorption of sulphuretted hydrogen gas*, and really seem to have been here and there employed for purifying coal-gas and for disinfecting cesspools (Zeitsch. chem. Grossgew. i. p. 70). This, however, cannot be done extensively, as the cinders do not act any thing like so energetically upon H_2S as precipitated ferric hydroxide or bog-iron-ore, and therefore the purifying apparatus would have to be made of enormous dimensions. Probably more success will be obtained in the manufacture of copperas for neutralizing the sulphuric acid formed in the oxidation of bituminous lignite slates; formerly metallic iron used to be employed for this purpose.

Iron.—It is quite possible to make good iron from pyrites-cinders; but the expense of doing this in most cases is too great; and very little of it has been made until the last few years. In 1873 the Chauny works exhibited iron made from non-cupreous pyrites-cinders, desulphurized by repeated roasting in a Perret's kiln in thin layers. For this purpose the plates of this kiln were charged alternately with cinders and with fresh pyrites, the heat produced in the burning of the latter causing a supplementary roasting of the cinders (Hofmann's 'Bericht,' 1875, i. p. 164).

Richters (Dingl. Journ. cxcix. p. 292) pursued the application of pyrites-cinders in a coke blast-furnace by the analysis of all the products. With a charge of 38 calcined magnetic iron-ore, 1½ black band, and 25·5 cinders (composed as on p. 175—that is, containing 4·35 per cent. SO_3 and 1·53 S in other forms), and 35 limestone, under especially favourable circumstances, pig-iron with only 0·022 per cent. of sulphur was obtained; when, however, the temperature was lower, even with only 12 pyrites-cinders to 53·5 other iron-ore and 33·5 limestone, the pig-iron showed 0·049, 0·088, 0·096, 0·224 per cent. of sulphur. With a mixture of 19·2 pyrites-cinders, 46·5 other iron-ores, 30·1 limestone, and 4·2 potsherds the sulphur in the pig-iron varied from 0·033 to 0·060 per cent.; by adding another 3·77 potsherds the sulphur was increased to 0·110–0·146 per cent. The pig-iron poorer in sulphur always contained a great deal of silicon, up to 3·485 per cent.

The cinders from roasting Schwelm pyrites (Chap. IV., p. 90) are said to furnish an excellent material for Bessemer pig, as they contain very little phosphorus and copper, which are so injurious to the quality of steel. F. Schmidt (Berg- u. hüttenmänn. Zeit. 1878, p. 68) states the composition of these cinders as follows:—

Ferric oxide	90·547	=65·0056 Fe.
Ferrous oxide	0·520	
Iron bisulphide	0·574	
Lead sulphide	0·142	
Copper sulphide	0·026	
Manganous oxide	0·463	
Carry forward	92·272	

Brought forward ...	92·272
Alumina	1·448
Lime	0·388
Magnesia	0·220
Sulphur trioxide	1·110
Phosphorus pentoxide	0·035
Silica	3·447
Moisture	0·897
	99·817

P. W. Hofmann ('Zeitschr. d. Vereins deutscher Ingenieure,' xviii. p. 521) has proposed the following process for utilizing the cinders from Westphalian pyrites. He found (like others) that this is very difficult to desulphurize, owing to its zinc, which sometimes amounts to 6 per cent. The cinders contain the zinc as sulphate, which is only decomposed at a much higher temperature than is attainable in a pyrites-burner. The zinc sulphate can be washed out by water at 40°; but it contains too much iron sulphate to be saleable. If, however, a solution of 1·25 sp. gr. be mixed with a proportion of NaCl equivalent to the sulphuric acid contained in it, and heated to 30° C., a lye of 1·38 sp. gr. is obtained, from which, on cooling, such a quantity of Glauber's salt crystallizes that this alone pays all expenses. The mother-liquor contains chloride of zinc with more or less common salt and the sulphates of iron, zinc, and sodium. If evaporated to 1·60 sp. gr., all foreign salts are separated, and a solution of zinc chloride, with mere traces of sulphates and of iron, remains behind, which can be employed directly for pickling railway-sleepers. The residue from lixiviating the sulphates is allowed to lie a few days in the air to dry; most of it then falls to powder. When this is passed through a sieve, the fine dust is found to be almost free from sulphur, the rougher particles containing nearly all the sulphur in the shape of FeS. The dust might be employed in a blast-furnace.

At the Aussig works formerly the crude zinc sulphate obtained in just the same way was worked up by the addition of calcium chloride (waste lye from the recovery of sulphur) into "pearl hardening" and zinc chloride. Owing to the want of a sufficient market, this manufacture has been discontinued.

The different sorts of pyrites behave very differently as to their desulphurization. Some of them can be roasted directly in the burners to such an extent that they may be used in iron-smelting. This is especially possible in the shelf burner of Malétra; the cinders from this are regularly smelted in mixture with other ores, not merely in the case of the Schwelm ore (see above), but in other cases also, since the sulphur in the ore can be brought down to less than 1 per cent. in these burners.

It has frequently been attempted to employ the cinders of small ore in larger quantities for smelting in a blast-furnace without stopping it up, by conglomerating them in different ways, but without much success. A patent has very recently been taken out by J. Cahen for this purpose (10th June, 1875). He moulds the cinders into suitable cakes with tar, peat, and limestone, and smelts these in a blast-furnace; the pig-iron is said to be very pure, the sulphur being absorbed by the lime, and the peat assisting in the formation of volatile phosphuretted hydrogen (?). J. L. Bell also moulds the small ore with lime into bricks, which gain hardness by drying, and uses them in a blast-furnace. All such artificial conglomerates are soon crushed by the great pressure in the blast-furnace, and thus act like the loose powder.

In the flue-dust and the chamber-deposit of many descriptions of pyrites the rare metals *selenium* and *thallium* have been found. The former has hitherto no industrial application, apart from the employment of crystalline selenium in photometry, as its electrical conductivity changes in proportion to the intensity of the light that falls upon it.

Thallium, however, is manufactured on a comparatively large scale at Aussig and Mannheim; and it might possibly be found useful for optical glass, replacing the alkali; owing to its very high atomic weight (204) it gives, along with red lead and quartz, the specifically heaviest and consequently the most refractive glass hitherto known (Lamy).

The preparation of thallium from the flue-dust of Westphalian pyrites has been described by Schaffner (Wagner's Jahresb. 1871, p. 1). The flue-dust was collected in a large brick chamber without being exposed to the action of nitrous vapours, the chambers being fed directly with nitric acid. It is coloured by ferric oxide, contains much arsenious acid, ferric sulphate, some zinc oxide, lead oxide, traces of antimony and silver, thallium sulphate, &c. Carstanjen (Wagn. Jahresb. 1868, p. 10) found in it 3·5 per cent. thallium. On the sides of the chamber crystals were found of the compound As_2O_3 and SO_3, discovered by Reich. The flue-dust is lixiviated by boiling with steam, with the addition of a little sulphuric acid, as a portion of the thallium seems to be present as basic sulphate, which would escape solution. After settling, the clear portion is siphoned off and filtered through calico; the residue is boiled again. From the liquid the thallium is precipitated as protochloride. The very impure reddish precipitate is washed with cold water and converted into sulphate by hot concentrated sulphuric acid, the heating being continued till all excess of acid is driven off. The sulphate is dissolved in water, filtered, and again precipitated by hyhrochloric acid, the TlCl now being separated almost in the pure state. If it is not yet pure, especially if it contains arsenic, the operation must be again repeated. In order to remove all arsenic, sulphuretted hydrogen is conducted into the solution of thallium sulphate, which precipitates all the arsenic with small quantities of thallium; the latter is precipitated from the filtrate by hydrochloric acid as perfectly pure TlCl, and converted into sulphate as above. The latter is reduced to metallic thallium by digesting its solution in a porcelain or stoneware dish with metallic zinc. The spongy metal obtained is washed with distilled water, pressed between blotting-paper, and melted in an iron or porcelain crucible, hydrogen or coal-gas being conducted through to prevent any oxidation; the heat should not be too strong, because it might volatilize the thallium. The melted metal, similar to mercury, is cast into small rods in paper moulds. It should be kept in boiled water free from air, the glass being closed whilst the water is boiling; but even then the latter after a short time shows an alkaline reaction. It is best kept in a solution of zinc sulphate. It can also be obtained well crystallized by Woehler's process, viz. by suspending in the thallium solution a beaker with its bottom cut off, and its lower part closed with bladder tied round: this is filled with water up to the level of the solution outside; a zinc plate is hung up in the water, and the latter connected with a platinum wire, which dips into the thallium solution and is bent into a spiral below the bladder.

Krause (Dingl. Journ. ccxvii. p. 323) observes that the treatment of thallium protochloride with concentrated sulphuric acid is very unpleasant work in large quantities. He has found that the decomposition can be quickly and completely effected by a weak solution of Glauber's salt, say 4° to 7° Tw. He lixiviates the fine dust in a cask with water and steam, siphons off the settled liquid into a second cask, and adds to this solution of thallium sulphate hydrochloric acid; the TlCl subsides very quickly, if the liquid is well agitated, for instance by a current of air. After a short rest the clear liquid is run off, the cask is filled up with pure water, heated by steam, and crystallized sodium sulphate added till the solution shows 7° Tw. After strong agitation the decomposition is complete, and the liquid is siphoned off into a third cask, which is placed somewhat lower; here it is acidulated with sulphuric acid, and the thallium precipitated by zinc. Similarly to Schaffner, he washes the sponge with water free from air, presses and melts it. This process permits working continuously and without contact with fire.

Nietzki has made very detailed communications on thallium (Wagner's Jahresb. 1876, p. 4). He found in the flue-dust of the Duisburg chemical works, where Westphalian pyrites is used, 0·1 to 0·2, sometimes even 1 per cent. thallium. The precipitation as TlCl is incomplete: to be sure TlCl, which is soluble in 500 parts of water, is much less so in the large excess of hydrochloric acid actually employed; but there remains even then 10 per cent. of the thallium present in the mother-liquor. Much more complete is the precipitation of thallium by potassium iodide as Tl I, even from very dilute solutions of flue-dust. Therefore both the mother-liquors from the TlCl precipitate and the dilute extractions of flue-dust are afterwards treated with KI. By boiling the Tl I with sodium sulphide the iodine is recovered as NaI; and the insoluble Tl_2S is worked up for Tl_2SO_4 along with the TlCl. From the sulphate the thallium is obtained by electrolysis, to avoid its contamination with zinc. In this case crude thallium sulphate can be employed; whilst direct reduction with zinc is troublesome, owing to the evolution of arseniuretted hydrogen and the reduction of ferric salts, the ferrous sulphate soon forming a crust over the zinc and making it inactive. Nietzki even employs KI for volumetrically estimating thallium; but the solutions must not be too dilute.

Stolba's process (Wagner's Jahresb. 1874, p. 1), allowing a thallium-alumina or thallium-iron-alum to crystallize from concentrated solutions of flue-dust, is only adapted for a substance extraordinarily rich in thallium.

Woehler (Ann. Chem. Pharm. clxiv. p. 74) states that thallium is more simply produced by fluxing the chloride with sodium carbonate and carbon. 20 parts TlCl, 8 parts of dry Na_2CO_3, and 1 part of lampblack are mixed together and fluxed in a fire-clay crucible at a moderate red heat. A small loss occurs by some chloride volatilizing; this can be avoided by stirring up the mixture with water, drying, and then fluxing.

Selenium was discovered (in 1817) by Berzelius in the chamber-deposit of the sulphuric-acid works at Gripsholm, at which Fahlun sulphur (obtained in roasting ores) was used. It also occurs in volcanic sulphur, *e. g.* 0·264 per cent. in the solfataras of Naples, according to Phipson (Chem. News, v. p. 337),—principally, however, in the Harz pyrites; so that the chamber-deposit of the Mansfeld and Oker works is the best source of it. Selenium always occurs in very small quantities; but its characteristic reactions cause it to be easily discovered, and it becomes very much concentrated in the deposit of flue-dust. Some Harz works' deposit is said to contain 10 per cent., that of the Eisleben works 9 per cent. of selenium; annually several cwt. are obtained in this way (Böttger and Kemper, Wagner's 'Jahresb.' 1860, p. 169). On selenium in French sulphuric acids communications have been made by Kuhlmann, Personne, and Scheurer-Kestner (ib. 1872, p. 246).

Selenium occurs in several allotropic modifications, in regard to which we must refer our readers to the chemical treatises. The statements are partly contradictory, and possess no technical interest. Its spec. grav. is given as 4·26 to 4·8, melting-point 400°, boiling-point about 700°.

The deposit contains free selenium, as the selenious acid formed by burning is reduced by sulphurous acid. Otto (Lehrbuch d. Chem. 4th ed. i. p. 633) digests the deposit, previously washed with water, with aqua regia to oxidize the selenium, adds sulphuric acid, evaporates to dryness, driving off the other acids, treats the residue with water, and from the solution, by cautious addition of ammonium sulphite, first precipitates white mercurial chloro-seleniate, then from the filtrate, by more ammonium sulphite and sulphuric acid, the selenium itself. From the mercurial precipitate the selenium can be obtained by oxidizing with nitric acid, evaporating, neutralizing with sodium carbonate, fluxing with potassium nitrate, boiling with hydrochloric acid in order to reduce SeO_3 to SeO_2, and precipitating the selenium from the solution by SO_2.

Liebe (Wagner's Jahresb. 1860, p. 178) extracts the oxidized mass, after evaporation with sulphuric acid, with water, neutralizes with soda-ash, evaporates to dryness, mixes the residue with an equal weight of sal-ammoniac, calcines the mass in a porcelain dish (when the sal-ammoniac reduces the SeO_2), and washes with water, pure selenium remaining behind.

Böttger (Dingl. Journ. clxxvi. p. 405) extracts the selenium from the chamber-deposit washed with water by means of a concentrated solution of neutral sodium sulphite, and filters it into dilute muriatic acid, which at once precipitates the selenium.

Otto (*l. c.*) quotes several other processes for obtaining selenium; but the newest communication is that of Nilson (Ber. d. deutsch. chem. Ges. vii. p. 1719) on the working-up of the Fahlun chamber-deposit for selenium. This cannot well be done by Otto's process; it is better to employ potassium cyanide, 2 parts of which yield 1 part of selenium. The washed deposit needs only to be digested with a concentrated solution of potassium cyanide at 80° to 100° C. till its red colour has just been turned into pure grey; the residue is washed with boiling water, filtered, and hydrochloric acid added to the solution; selenium at once precipitates in cherry-red flakes, as the liberated selenocyanic acid is almost instantaneously decomposed into selenium and hydrocyanic acid; the sulphur dissolved at the same time remains in solution as sulphocyanic acid. The selenium thus obtained contains only a little copper, iron, and perhaps traces of mercury: it is obtained quite pure by dissolving in nitric acid, evaporating to dryness in a water-bath, subliming the anhydride in a current of dry air, and treating its solution with sulphurous and hydrochloric acids.

The Mansfeld Kupferschiefer Mining Company (Wagner's Jahresb. 1876, p. 297) in 1875 produced

Flue-dust containing selenium	2378 kil.,	value £18.
Selenium	4½ „	„ £ 6 2*s*.

The extraction of Copper from Pyrites-cinders.

This manufacture cannot properly be regarded as a by-work done in sulphuric-acid making; with as much, if not with greater right, the latter might be considered a secondary branch of the extraction of copper, since in the cupreous ores the value of the copper mostly exceeds that of the sulphur contained in them; but if the value of the final products be counted, that of the sulphuric acid certainly mostly far outweighs that of the copper. Even in the large English works now-a-days the extraction of copper from the cinders is rarely done in the chemical factory itself; the former is concentrated in a few works erected in the centres of the chemical trade, which receive the burnt ore from a whole group of chemical works. One of the largest pyrites-mining companies, the Tharsis Sulphur- and Copper-extracting Company, supplies its ores to the consumers only on condition of returning the burnt ore to the copper-works belonging to the same Company. A similar establishment was founded a short time ago at Duisburg by a number of Rhenish manufacturers, likewise based on the extraction of Spanish-pyrites cinders. Although the production of copper thus does not belong to the usual cycle of vitriol- and alkali-works, yet it is most intimately connected with it, especially in Great Britain; and a short description of that production does not seem out of place here.

The percentage of copper in the ores in question (comp. p. 98) is mostly so small, rarely above 4 per cent., that its extraction by smelting would not pay. This can only be made possible at the outset by carrying on the first necessary operation (the calcining or burning) in such a way that the calcining gas does not go away into the air, but is taken into lead chambers and sulphuric acid made of it, which helps to pay for the ore. But something else is necessary in practice. The cinders from burning the ore are still too poor in copper to be smelted in the usual way. They might possibly be smelted to coarse metal, with a mixture of a little 'green pyrites, siliceous sand, and slags; and this coarse metal might be sent to copper-works for further treatment; but in that case only a portion of the copper would be obtained, and the expense would be barely covered. When the quantity of poor ore coming into the market became larger, this way of utilizing it was out of the question. Other drawbacks in smelting for coarse metal, as they were observed at Oker, will be mentioned below.

Accordingly, since 1865, the copper of poor ores is always extracted *in the wet way*. From immemorial times the pit-waters arising from weathered ore have been precipitated by metallic iron, and *cement copper* obtained in this way; but the processes for converting the copper purposely into such compounds that it becomes capable of being dissolved and precipitated, all date from a recent period. Exact descriptions of the former processes are found in

Percy's 'Metallurgy,' more recent processes in Stölzel's 'Metallurgie,' i. p. 714, and in Hofmann's 'Bericht' of 1873, p. 885 (this article is from the pen of Professor Kerl). Most of the volumes of Wagner's 'Jahresberichte' contain the literature of this branch.

It is beyond the scope of this book to enter specially upon all the proposed or really carried-out processes for copper-extraction in the wet way; we must refer the reader to the authorities just mentioned, and we shall only describe that process which for a number of years has been exclusively employed for working up the cinders from vitriol-works, viz. the *chlorinating calcination,* followed by the *precipitation by means of iron.* It appears that the interesting process of lixiviating by means of ferrous chloride, originally proposed by Schaffner, but generally called after Sterry Hunt and Douglas, is not in use at vitriol-works or at the copper-works in immediate connexion with these; we must therefore, in respect of this also, refer to the originals.

The first attempts in this way seem to be referable to Hunt (patent of Jan. 21, 1840), and especially to Longmaid (patents of Oct. 20, 1842, and Jan. 1, 1844). The latter exactly described the principles of the process, as it is carried out to-day, certainly with a view to making salt-cake and chlorine as the principal products; and he also worked it out on a large scale; so that he must be regarded as the founder of the wet extraction of copper. Certain small improvements were patented at different times—for instance, by Gossage on July 17th, 1850. We find much later, in 1856, the process started with a good deal of noise as a novel one, by Bechi, of Florence, and Haupt, of Freiberg, for working the ores at Capanne Vecchie (Wagner's Jahresb. 1858, p. 68). It is strange that, 16 years after Longmaid, such a distinguished metallurgist as Gruner could ascribe the success of Bechi's process less to the influence of the common salt than to the fine grinding. Bechi and Haupt's process was patented in England in the name of Hähner on March 7th, 1856; it differs from Longmaid's process merely by much greater complication, such as calcining three times instead of once, and has long since been given up. Schaffner (Wagner's Jahresb. 1862, p. 119; 1871, p. 139) improved the process in several respects; but it was carried out on a large scale chiefly in England, by Phillips, Henderson, Tennant, and others.

Spongy iron was first employed by Gossage; it was again patented by Aas in 1861, and again by G. Bischof in 1862.

The process now generally employed in England has been principally described by Clapham (Chem. News, xxiii. p. 26), Wedding and Ulrich (Wagner's Jahresb. 1872, p. 152), Gibb (Chem. News, xxxi. p. 165, and several publications of the Tyne Chemical Society), by the author (Dingl. Journ. cciv. p. 288, ccxiv. p. 466, ccxv. pp. 54 & 229, ccxix. p. 323); the process at Oker by Bräuning (Preuss. Zeitschr. f. Berg-, Hütten- u. Salinenwesen, 1877, p. 156). In the following description the above sources are used, along with the author's notes taken at several copper-works.

The three most important ores employed in the English factories contain from 47 to 49 per cent. of sulphur, and the following quantities of copper and silver:—

	Copper. per cent.	Silver. ounce, troy, per ton.
Rio-Tinto	3·80	1·20
Tharsis	3·50	0·75
San-Domingo	3·70	0·75

(N.B. An ounce troy is =480 grains; there are 32,666 ounces troy to the ton.)

The "ordinary copper-ores" at Oker generally consist of 60 per cent. iron-pyrites, 23 per cent. copper-pyrites, 6 blende, 2 galena, 9 gangue (complete analysis, p. 114).

The percentage of sulphur in the cinders as they are supplied by the acid-works varies extremely; hardly ever falling below 2 per cent., it sometimes rises above 10 per cent. The latter, to be sure, results from very bad work indeed; but 4 to 5 per cent. is considered very fair work; and as much is indeed required for the wet copper-extraction, the sulphur may even amount to 1½ times as much as the copper, but no more. At Oker the cinders are delivered to the extracting works with 5 to 8 per cent. sulphur and 6 to 9 per cent. copper. If the pyrites arrives too well burnt from the acid-works, the copper-works add a little green pyrites in order to have sufficient sulphur for the first stage of their process.

The following analyses by Gibb show the composition of the pyrites-cinders as the copper-works receive them:—

	Rio-Tinto.	Tharsis.	Domingo.	(Norway).
* Copper	1·65	1·50	1·55	1·01
* Iron	3·64	3·23	3·76	3·33
* Sulphur	3·53	3·15	3·62	3·10
Cupric oxide	2·75	2·56	2·70	·39
Zinc oxide	2·02	·55	·47	6·46
Lead oxide	·47	·70	·84	·06
Silver	·0037	·0023	·0023	....
Cobaltic oxide	·007	·032	·033	....
Bismuth oxide	·013	·010	·013	....
Calcium oxide	·20	·25	·28	2·30
Ferric oxide	77·40	77·00	78·15	68·06
Sulphuric acid	6·10	5·25	5·80	6·56
Arsenic acid	·24	·17	·25	·05
Insoluble residue	1·45	5·85	1·85	8·74
	99·47	100·25	99·31	100·06

* Calculated as Cu_2S and Fe_2S_3.

Phillips states the following as the composition of cinders from San-Domingo ore:—

Sulphur	3·66
Arsenic	0·25
Iron	58·25 (=83·0 Fe_2O_3)
Copper	4·14
Zinc	0·37
Cobalt	trace
Lead	1·24
Lime	0·25
Insoluble	1·06
Moisture	3·85
Oxygen and loss	26·93

Wedding and Ulrich found in samples from Widnes (*a*) and Hebburn (*b*):—

	Sulphur.		Copper.	
	a.	*b.*	*a.*	*b.*
Altogether	4·12	3·75	4·08	5·75
Of this soluble in water	43 p. c.	37 p. c.	46 p. c.	26·1 p. c.
„ „ „ HCl	55	59	22·2	13·3
In the residue	2	4	31·8	60·6
	100	100	100	100

According to Hjelt the cinders from Spanish pyrites contain 0·19 per cent. arsenic.

The Oker cinders showed, on an average of a month's work:—

Copper (principally as CuO)	7·83 p. c.
Iron (principally as Fe_2O_3)	40·53
Lead (as PbO)	2·09
Silver	0·008
Zinc (as ZnO)	1·95
Manganese (as Mn_3O_4)	0·40
Sulphur	3·80
Sulphuric acid (corresp. to 3·8 S)	9·51
Alumina	4·43
Other gangue	11·65

The sulphur must be mostly in combination with iron, since unburnt crude ore could be seen as cores on breaking up the lumps. The sulphuric acid is partly combined with lime, partly with metals, probably, as may be inferred from the well-known processes of roasting, in the first line with CuO and ZnO, in the second line with FeO or Fe_2O_3. From this the following would appear to be the most probable composition of the cinders:—

CuO	9·80 p. c.	
Fe_2O_3	53·14	(=37·2 Fe)
FeS_2	7·13	(= 3·8 S)
PbO	2·25	
Ag	0·008	
ZnO	2·43	
Mn_3O_4	0·57	
SO_3	9·51	
Al_2O_3	4·43	
Other gangue	11·65	
	100·918	

These cinders were formerly utilized in small blast-furnaces 7 ft. high, the first smelting yielding a rich coarse metal (55 per cent.) and a little blister-copper. Higher furnaces could not be used, on account of the large percentage of Fe_2O_3, which would have been partly reduced. The drawbacks of this smelting were the short duration of the furnace-lining (47 to 72 hours), and great loss of metal by the slag and the flue-dust. Therefore, instead of smelting them, the cinders have latterly been worked up by the wet process.

The cinders are first *finely ground*, either by crushing-rollers or by edge-runners, and at the same time mixed with a sufficient quantity of *sodium chloride*, usually in its cheapest form, viz. rock-salt. This addition, where the furnaces are worked by hand, varies from 10 to 20 per cent., on an average it is 15 per cent. But with the mechanical furnace to be described below, only 7½ of salt per cent. of burnt ore are required. The ground mixture is passed through a cylindrical sieve with 8 holes to the inch; the coarse particles are sent back to the mill, where they are ground down completely, so that the mixture always remains the same. The whole being finely ground, it is filled into iron bogies and run on tramways over the calcining furnaces.

At Oker the cinders are mixed with 15 per cent. (formerly 20 per cent.) of Stassfurt potash salts (carnallite) and are ground down to the size of 2 millims. The Stassfurt salts contain the chlorides of magnesium, potassium, sodium, and calcium, all of which assist in the calcining process.

The *calcination* takes place in furnaces of very different kinds. These may be classed as follows:—

1. *Ordinary reverberatory furnaces*, similar to black-ash furnaces. These were in use at first, but have been given up long since.

2. *Reverberatory furnaces with gaseous fuel.* These are principally used in Lancashire; they are illustrated by figs. 284 to 287.

Fig. 284.

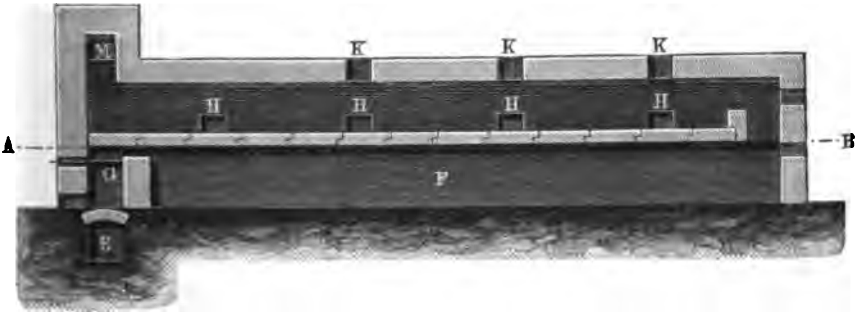


Fig. 285.

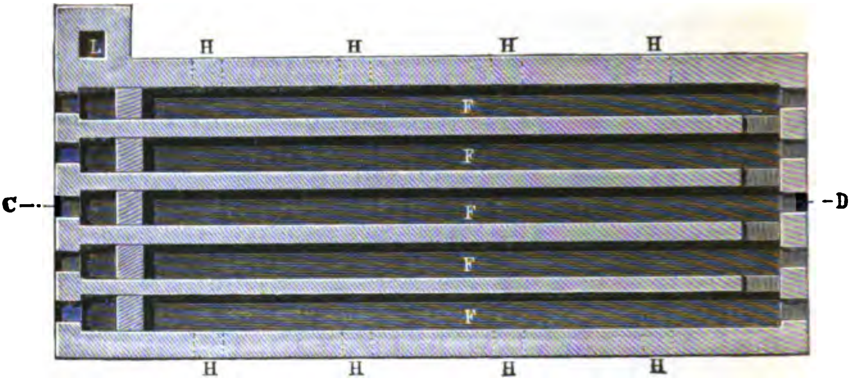


Fig. 286.

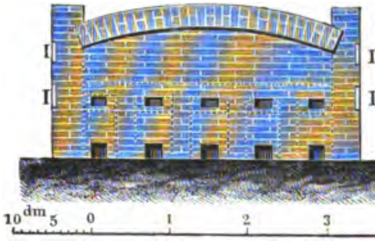
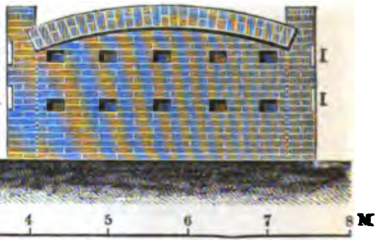


Fig. 287.



Three generators furnish the gas for eight calcining furnaces; it passes from the main flue into the flue E across the width of the furnace; from this it rises through 5 vertical flues G, each of them provided with a damper; it then travels through the flues F below the furnace-bed, then directly over the charge and through the outlet M to the condensers. The air for combustion is introduced by two tiers of holes with slides in each of the two furnace-ends (figs. 286 & 287), so that one of the tiers communicates with the flues below the bed, the other with the space above the fire-bridge. Thus the combustion can be regulated so that some unburnt gas gets as far as the fire-bridge and is only lighted there. H H are the working-doors; K, charging-holes in the arch, closed by loose metal plates and fine ore on the top of these; I, binding-plates. Each furnace holds 45 cwt. of ore.

Similar furnaces are used at Oker; these are represented in figs. 288 to 291. They work two charges of 2½ tons each every 24 hours.

Fig. 288.

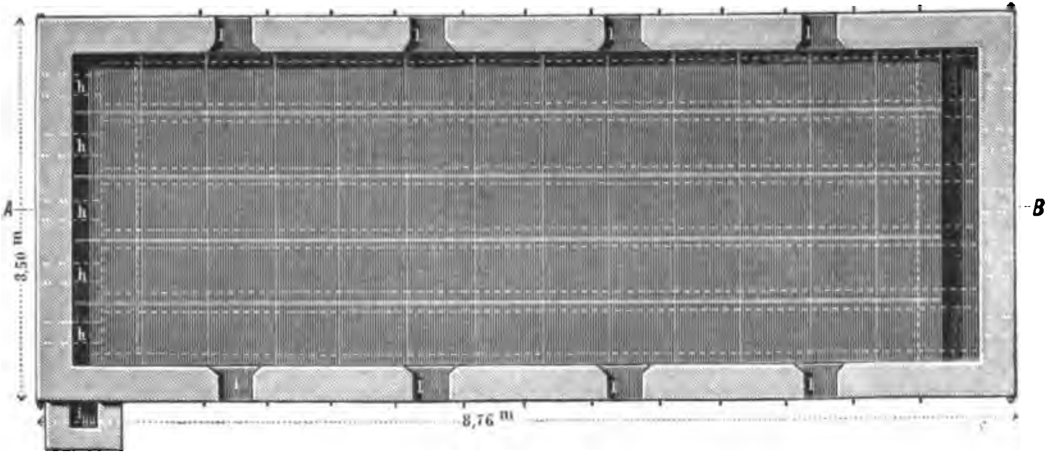


Fig. 289.

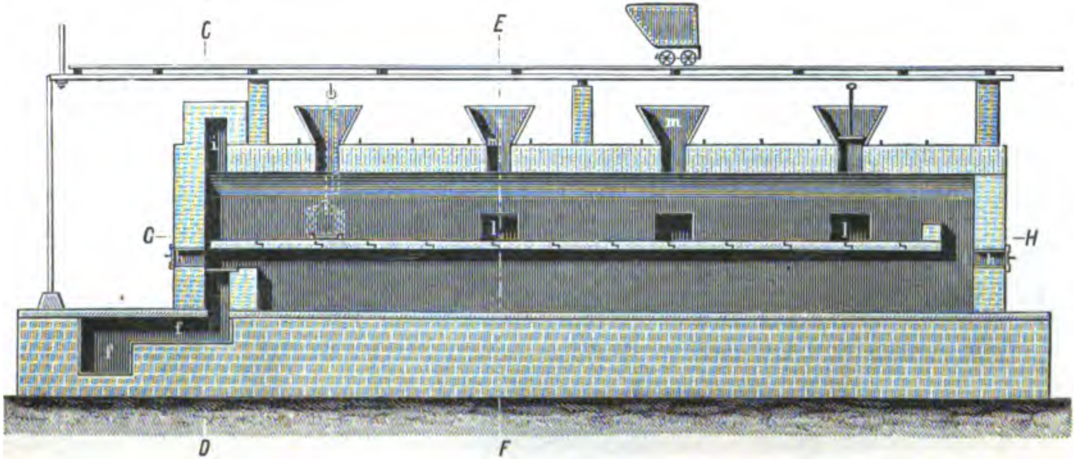


Fig. 290.

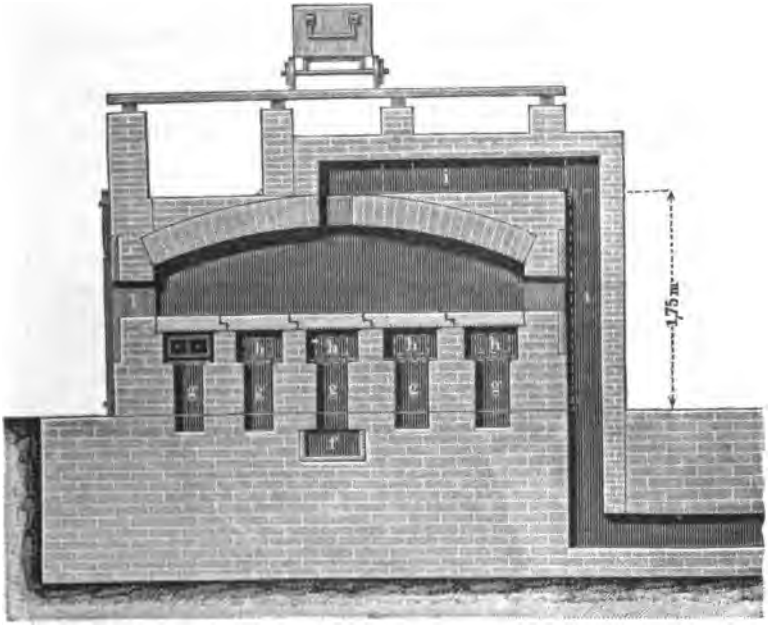
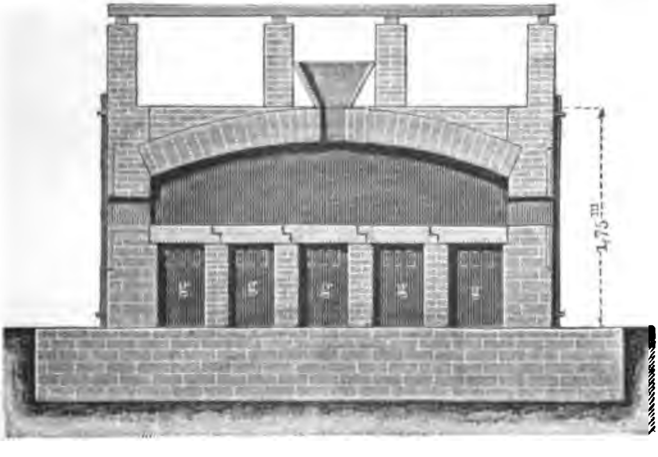


Fig. 291.



same below the furnace-beds; *h*, the slits for introducing the air; *i*, the outlet for the mixed fire- and calcining-gas to the condenser; *l*, the working-holes; *m*, the charging-hopper.

3. *Blind roasters* (muffles), employed at all the works of the Tharsis Sulphur and Copper Co., figs. 292 to 294. Here the flame

Fig. 292.

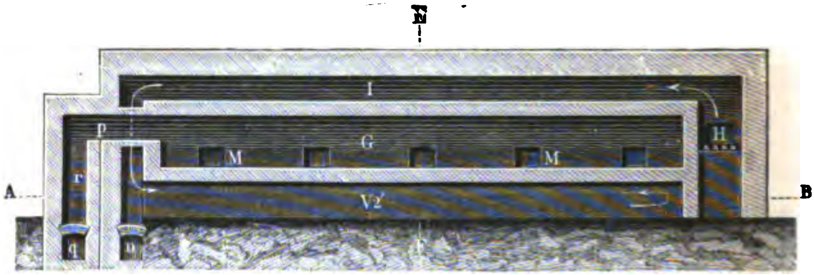


Fig. 293.

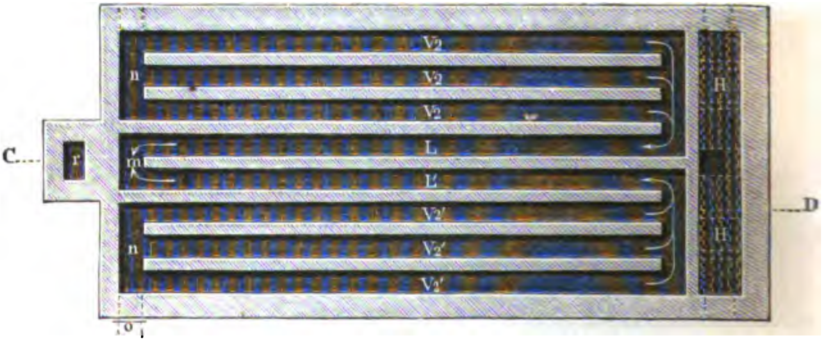
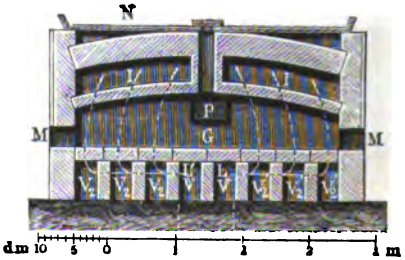


Fig. 294.



through the brickwork of the bed and the arch. The charge is worked in the muffle G, with the working- and discharging-doors M. Its bottom is formed by fire-clay slabs covering the fire-flues VL; its cover by a thin arch. The ore is spread in a thin layer, and receives the air necessary for its roasting only through the working-doors M; in the other part of the furnace the oxygen contained in the fire-gas is active as well. The flame from the double grate H first travels by I over the muffle-arch, then downwards in three channels on each side (V_2 & V'_2). The gas of each three channels is united in a flue (L & L′), and, after having returned in the opposite direction, descends by *m* into the flue *n* situated below the ground-line, which enters the main chimney. *o* is the regulating damper; *p*, the outlet for the calcining-gas, which descends by *r* to the horizontal subterraneous flue *q*, and thence arrives at the acid-condensers. The metal dish N, on the top of the furnace, serves for a first heating of the mixture; it communicates with the muffle through several pipes, usually covered with a metal plate; by raising the latter the mixture is let down into the muffle.

4. *Combined furnaces*, used by the Bede Metal Company at Hebburn-on-Tyne (shown in figs. 295 to 298). Here the flame of the

Fig. 295.

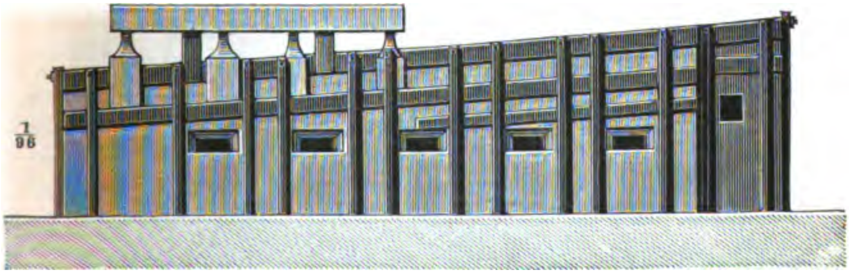
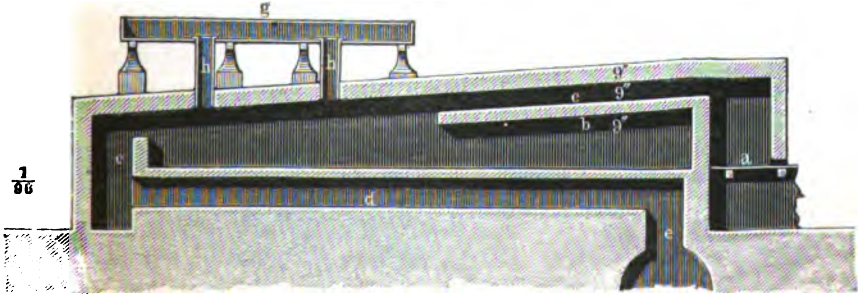


Fig. 296.



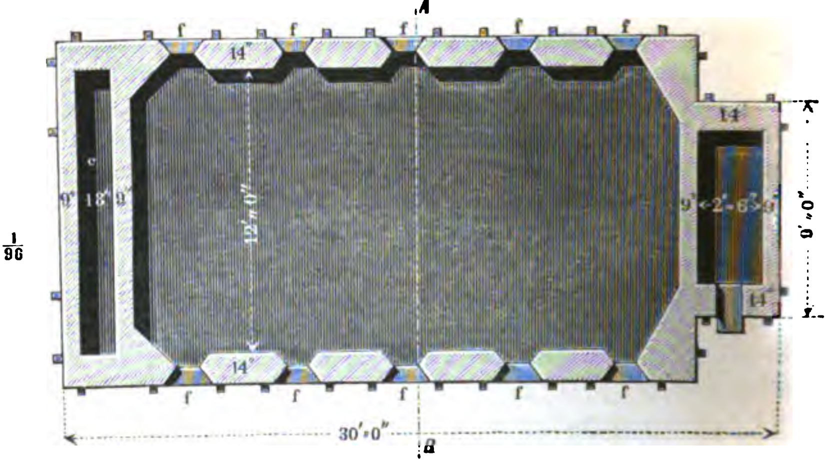
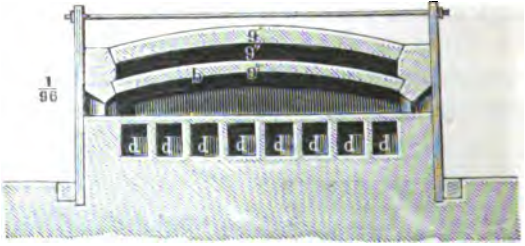
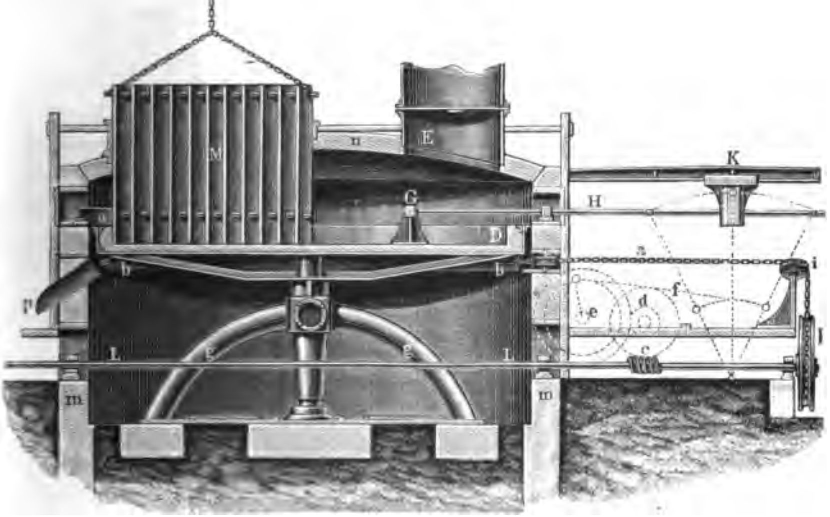


Fig. 298.



fire, *a*, does not play direct upon the charge, but is kept off it by an arch, *b*, reaching half the length of the furnace; after this the flame touches the furnace-bed directly and descends by *c* in order to return by 8 channels, *d d*, beneath the furnace-bed, and to escape at *e* into an underground flue leading to an acid-condenser. The working-doors *ff* serve for stirring and discharging; the pan *g* for a first heating of the charge; the pipes *h h* for dropping it into the furnace. The purpose of the arch *b* is to avoid overheating those portions of the ore nearest the fire-bridge, in which the copper might easily be roasted dead; in fact the hottest part of these furnaces is that behind, the part below the protecting arch hardly attaining a dark-red heat.

5. *Mechanical calcining-furnaces* with revolving hearth, patented in 1872 by Gibb and Gelstharpe, and 12 of which exist at the Bede metal-works. Figs. 299 to 302 represent this furnace. The bed



M
n
E
K
G
H
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b
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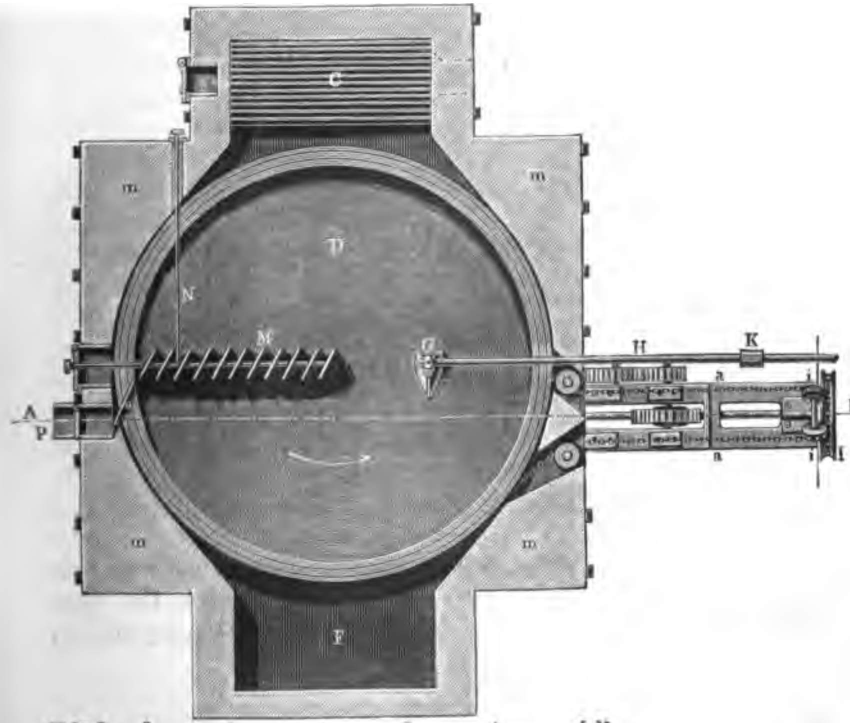
d
e
p
L
g
g
L
c
l
m
m

Fig. 300.



C
m
m
D
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l
i
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m
F
10 dm 5 0 1 2 3 4 5 M

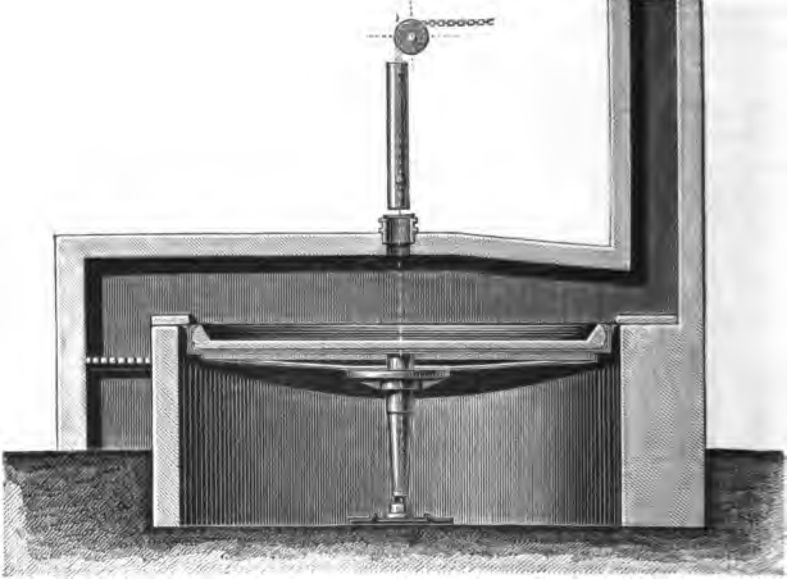
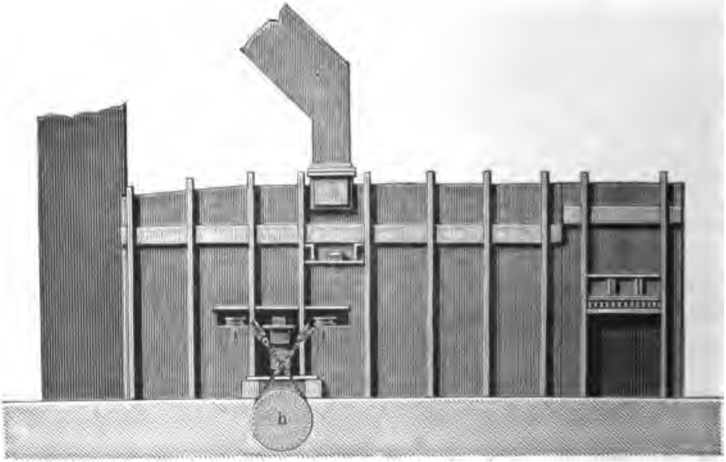


Fig. 302.



consists of a circular pan, *b b,* made of boiler-plate, lined with fire-bricks, D. The side walls (*m m*) and the arch (*n*) form the other parts of the calcining-space. On one side there is a fire-place, C, underground flue leading to the chimney, along with the gas evolved in calcining. The pan *b b* is carried on wrought-iron girders fixed on a central cast-iron spindle which works in a footstep and is maintained in a vertical position by a collar, fitted with brasses, in which an upper bearing of the spindle works, carried by the tubular cast-iron stays *g g*. This pan is caused to revolve in its own plane on the central footstep by an endless chain, *a*, carried round a sheave, I, from which it passes over the guiding pulleys *i i* to the horizontal sheave underneath the pan.

A small pump, driven by the same main shaft, constantly pumps lubricating oil from a tin vessel into the footstep, the excess of oil running back into the same vessel again. The hearth is traversed by a cast-iron plough, G, made to reciprocate in a radial line of the circle by the wrought-iron arm H connected with the cross head K. The motion of this cross head is equal to the radius of the hearth, and is derived from the driving-shaft L by means of the worm and scroll-wheel *c* and the pair of spur-wheels *d* and *e*, the larger of which, by means of the crank-pin and connecting-rod *f*, gives a reciprocating motion to a lever, the forked upper end of which, by means of pins working in slots, moves the cross head with the plough-arm and plough. The speeds of the circular hearth and the plough are so adjusted that the plough does not travel more than its own breadth during one revolution of the hearth; so that every part of the circle of the hearth is gone over by the plough in each journey from or to its centre.

The furnace is charged by means of the hopper E, let into a slit of the arch, and discharged by a set of parallel plates M, which are arranged obliquely across a radial line of the circle of the hearth on the opposite side of the centre to that in which the plough travels. These plates are rigidly bound together at top and bottom, and suspended by a chain, so that they can be raised out of or lowered into the furnace through the roof. The plates are shown in the furnace in the position for discharging, with a plate, *o*, fixed in the doorway, folded against the outer plate of the series M. When the discharging-plates are in this position, each throws the ore carried against it by the revolution of the hearth towards the circumference into the path of the next outward plate, by which it is again thrown outwards at the next revolution, to be at length propelled against the doorway-plate *o*, which throws it from the edge of the hearth

When the furnace is working, the plates are raised through the roof, and the opening through which they pass is closed by a slide. The bolt N fixes the plates in their position.

In order that the pan may freely revolve round the spindle, the side walls *m m* are 1 inch apart from the edge of the pan; the air rising in this intermediate space causes the oxidation. The brickwork reaches down to the ground-line; and the machinery underneath the hearth is only accessible by an iron door, so that it is protected from the coal- and ore-dust. Every part of the machinery is very strong, and not liable to get out of repair—excepting the cast-iron plough, G, which must be replaced once a fortnight, but at a smaller expense than that of the tools in a furnace worked by hand. The plates M suffer very little, because they are only for a very short time exposed to the fire. The twelve furnaces at the Bede Metal-works are driven by two steam-engines of 18 indicated horse-powers each.

All these different descriptions of furnaces have the same object; and the *style of working* is accordingly very similar in all cases. The ore must, of course, be completely roasted—that is, sufficiently to convert the copper into sulphate, which, owing to the presence of sodium chloride, at once forms with this, by mutual decomposition, cupric chloride and sodium sulphate; whilst the iron should be converted as completely as possible into ferric oxide, so as to become insoluble. In this process, owing to the simultaneous action of SO_3 and O upon NaCl, chlorine is evolved, which must greatly aid in chlorinating the copper as well as any other metal present. At the same time, principally HCl is formed, which converts the oxides of copper, silver, zinc, &c. into chlorides, whilst at the calcining-temperature ferric chloride cannot continue to exist as such. At Oker the formation of hydrochloric acid is purposely aided by using carnallite in lieu of common salt, as the $MgCl_2$ contained in the former readily yields MgO and HCl. This, however, is not absolutely requisite, as with 2 NaCl the $CuSO_4$ already produced in calcining yields $CuCl_2$ and Na_2SO_4. Cu_2Cl_2 also is always formed at the same time. Since the chlorides of copper are both unstable and volatile at very high temperatures, a low red heat ought not to be exceeded; so that any copper-pyrites still present in the cinders is not burnt, and therefore escapes chlorination. Accordingly, copper-pyrites (or Cu_2S) ought not to be present in any quantity than 8 per cent. of copper, which can never be roasted with sufficient completeness in the chemical factories, cannot be utilized by this process, but only by smelting.

Manifold experience has taught that without employing common salt (that is, without chlorinating) it is never possible, even approximately, to hit the point where the more easily decomposed ferric sulphate no longer exists, whilst the less easily decomposable cupric sulphate is still present as such, the iron being then present in an insoluble, the copper in a soluble form. If ferric salt remains in a soluble form, it naturally passes over into the lyes, and, in the operation of precipitating the copper, causes a great loss of metallic iron by its reduction to ferrous salts. If, on the other hand, much copper has likewise passed into an insoluble form, more muriatic acid is required for its solution. In any case the formation of some cupric oxide and cuprous chloride, insoluble in water, cannot be avoided.

Wedding has observed, and described in detail, the calcining process as carried on at Widnes in a gas-furnace. The charge, of 45 cwt. of ore mixed with 17 per cent. of salt, is let down onto the hearth, spread out and slowly heated till a low red-heat has been reached nearest the fire-bridge; the charge is turned over and left to itself, the gas being shut off, but the air being allowed to enter, so that after two hours scarcely any glowing can be perceived at the fire-bridge. After one hour's and three hours' calcining respectively, the copper of the charge behaved as follows :—

	1 hour's calcining. per cent.		3 hours' calcining. per cent.
Soluble in water	54	...	51
„ HCl	38	...	42
„ NO_3H	8	...	7

After three hours the charge is quite dark, and is now well turned over with a slice of 3 or 4 inches breadth, as well as with a rake; there ought to be no necessity for giving more fire, as the temperature should from the first have been raised to the proper point. On raking over the charge, which is now done regularly with short interruptions only, the temperature rises of itself in consequence of the chemical reactions, the rise becoming sensible after 4¾ hours (counting from the beginning); so that after 5¼ a copious evolution of white vapours and blue flames; from this period there is less of these, and it is the calciner's principal task to see that the heating of the charge is quite equal all over, and that some places do not show more blue flames than others. After 6½ hours these flames are almost entirely gone; and this fact, along with the greenish-grey colour of the charge, are the practical tests for judging whether the operation is finished. A sample is now drawn; and if its examination shows the completion of the calcining-process, the charge, which has now been 6½ or 6¾ hours in the furnace, is drawn out. Of the copper now

75 per cent. is soluble in water,
20 „ „ HCl,
5 „ „ NO_3H.

Good workmen can finish the calcining in a gas-furnace in six hours.

Wedding observes that the watery solutions constantly show more sulphur, and that the testing of the calcined ore of different works proves the process to be carried out very unequally; but it is certain that the best results are in fact got by the most careful work. The calciner's task is, first to heat the charge and thus to start the chemical reactions, but then to maintain these at the lowest possible heat up to the finish, and to spread them equally through the whole mass. It is of great importance not to leave the ore any longer in the furnace than exactly the necessary time; this is made difficult by the depth of the layer of ore, viz. 5 or 6 inches —which, on the other hand, facilitates the chlorination, since the gas rising in the ore heated both at top and bottom has all the more opportunity of coming into contact with all parts of it.

Evidently the process is altogether dependent upon the skill of the workman, whilst with the mechanical furnace of Gibb and Gelstharpe only the firing needs attention. In the latter furnace indeed a lower heat is sufficient, one that never reaches a red glow visible in daylight.

At Oker, where gas-furnaces exactly like those at Widnes are used, each charge of 50 cwt. of ore with 15 per cent. potash salts is brought to a low red heat in four hours; the firing is then interrupted and the mass raked over. Owing to the chemical reactions, During the turning-over stage, which lasts five hours, the air-slides are opened to admit the air to the charge; after that time the charge is drawn. Two charges are put in every 24 hours. Analysis of a sample taken in the middle of the calcining-process (the mixture containg 20 per cent. carnallite) :—

Soluble in water.

	per cent.			per cent.
Cu	1·94,	calc. as	$CuCl_2$	3·11
Ag	0·003,	„	$AgCl$	0·004
Fe	0·74,	„	$FeCl_2$	1·68
Al_2O_3	0·11,	„	$Al_2(SO_4)_3$	0·39
Mn	0·69,	„	$MnCl_2$	1·58
Ni	0·20,	„	$NiCl_2$	0·44
Zn	1·60,	„	$ZnCl_2$	3·40
CaO	2·76,	„	$CaCl_2$	6·27
MgO K_2O Na_2O		„	Sulphates	18·15
				35·024

Insoluble in water.

	per cent.			per cent.
Cu	4·32,	calc. as	CuO sol. in HCl	5·12
			Cu_2S sol. in aqua regia	0·29
Pb	0·39,	„	$PbSO_4$	0·57
Fe	34·49,	„	Fe_2O_3	45·38
			$Fe_2(SO_4)_3$	3·27
			FeS_2	2·64
Al_2O_3	3·30,	„	Al_2O_3	3·30
Mn	0·03,	„	Mn_2O_3	0·04
Zn+Ni	0·29,	„	ZnO+NiO	0·36
CaO	0·45,	„	$CaSO_4$	1·09
SO_3	1·86			
S	1·47			
Cl	trace.			
Insoluble in acids				2·96
				65·02

Sample of calcined ore taken at the finish :—

Soluble in water.

	per cent.			per cent.
Cu	3·86,	calc. as	$CuCl_2$	8·17
Ag	0·005,	„	$AgCl$	0·006
Fe	0·60,	„	$FeCl_2$	1·38
Al_2O_3	0·17,	„	$Al_2(SO_4)_3$	0·56
Zn	1·64,	„	$ZnCl_2$	3·42
Mn	0·75,	„	$MnCl_2$	1·71
Ni	0·07,	„	$NiCl_2$	0·15
CaO	1·60,	„	$CaCl_2$	3·17
MgO K_2O Na_2O		„	Sulphates	20·50
				39·066

Insoluble in water.

	per cent.			per cent.
Cu	2·57,	calc. as	CuO	3·18
			Cu_2S	0.03
Pb	1·17,	„	$PbSO_4$	1·26
Fe	34·56,	„	Fe_2O_3	47·91
			$Fe_2(SO_4)_3$	1·02
			FeS_2	1·18
Al_2O_3	0·44,	„	Al_2O_3	0·44
Zn	0·37,	„	ZnO	0·46
Mn+Ni	trace.			
CaO	0·49	„	$CaSO_4$	1·19
SO_3	1·49			
Cl	trace.			
S	0·64			
Insoluble in acids				3·69
				60·36

The mechanical furnace has the advantage also in respect of the addition of salt; only 7½ per cent. of salt is required in it, against 15 in the hand-furnaces. Often only a portion of the salt is mixed with the ore at the outset, and the remainder added afterwards. In the blind roasters the ore is calcined first nine hours with 12 per cent. salt, and another three hours with 8 per cent. more salt. In the combined furnaces with protecting arch the weight of ore is 58 cwt., and the time of calcining eight hours; in the mechanical furnaces 5 tons and nine hours.

Gibb gives the following analyses of the results of calcination:—

	Gas-furnace.		Close furnace.		Mechanical furnace.	
	p. c.	Cu p. c.	p. c.	Cu p. c.	p. c.	Cu p. c.
Cupric chloride ...	4·03	= 1·90	4·25	= 2·00	6·70	= 3·15
Cuprous chloride...	·32	= ·20	·35	= ·21	nil	
Cupric oxide.........	1·26	= 1·00	·88	= ·70	·32	= ·25
Sodium chloride ...	2·50		3·40		0·90	
Sodium sulphate ...	13·18		17·40		14·03	
Insoluble copper ...		·15		·12		·13
Total copper......		3·25		3·03		3·53

The principal point is always this, that as little copper as possible should remain in a state insoluble in water and dilute acids. In the above cases the quantity varies from 0·12 to 0·15 per cent.; the slightly more favourable result of the blind roaster, according to Gibb, is far more than counterbalanced by its greater consumption of fuel (50–100 per cent.). The most favourable result is obtained with the mechanical furnace, in which next to no cuprous chloride and, even with the worst ores, rarely more than 0·25 per cent. of CuO are formed.

At Oker the average result of the constantly taken samples of calcined ore is this: 75 per cent. of the copper contained in the ore is soluble in water, 20 per cent. in dilute muriatic acid, and 5 per cent. in aqua regia.

If the pyrites contains more than 4 per cent. copper, the cinders in England cannot be worked with advantage by the wet process. At the Bede Metal-works many experiments have been made with richer ores; but with 6 per cent. copper the salt, the coals, and the labour are already too dear. In this case, however, another circumstance comes into play: by the Cornish copper assay about 2 per cent. copper less than the truth is indicated; and this with a poor ore of course amounts to a much larger proportion of the whole (sometimes more than half) than with richer ores; thus the former are cheaper for the wet process than the latter. In the Harz, where this reason does not exist, ore up to 8 per cent. Cu can be extracted by the wet process.

It has already been remarked that the sulphur in the cinders must bear a certain proportion to the copper; with a 4-per-cent. ore it ought not to exceed 6 per cent.; an equal percentage of S and Cu is preferable. If less S is present, raw pyrites must be added. The more S there is present, the more salt must be added, and the more time will the calcination take.

The *tests* for ascertaining the completion of the calcination are of a very simple character, which is all the more necessary as they must be made very quickly. A certain *measure* of the charge, not weighed, is lixiviated by water and dilute HCl, just as on the large scale; the residue is boiled with aqua regia, supersaturated with ammonia, and allowed to settle; the more or less blue colour of the solution of ammonio-cupric salt gives a sufficient indication of the percentage of insoluble copper.

Condensation of the calcination-gas.—In all the descriptions of furnaces mentioned above, except the blind roasters, this gas is mixed with the fire-gas; but even in these it is mixed with air to such an extent that a condensation of strong acid is not very well possible. The acid is a little more concentrated than that from open calciners; but this matters very little, as it is always used in a very dilute state for lixiviating. The calcination-gas principally contains (beside oxygen and nitrogen) SO_2, SO_3, HCl, Cl, and very small quantities of metallic chlorides. Henderson had proposed to volatilize the copper entirely as $CuCl_2$, and condense the latter in towers; but this has turned out quite impracticable. The small quantity of copper passing over into the condensers, about $\frac{1}{4}$ per cent. of the whole, is not lost, as the condensed acid is used for lixiviating the charge.

The condensation of the gas from the calciners takes place in towers of exactly the same kind as those (described in detail later on) for muriatic acid—that is to say, made of brickwork set in tar and sand (or, better, of stone flags), and packed with coke, fire-bricks, and the like. Coke can be used with blind roasters; but the other furnaces require bricks &c., and must have larger condensers, as these have to serve for a larger volume of gas. The size of the towers varies with that of the plant; for 12 furnaces a tower of 8 feet square and 40 to 50 feet high is sufficient. The gas enters at the bottom, meets a spray of water coming from the top, which washes the acids out of it, and again leaves the tower at the top, whence it is taken downwards into a flue leading into the chimney.

The total condensed liquid (a mixture of weak sulphuric and muriatic acids; the SO_2 in the condensation is oxidized to SO_4H_2 by the action of the chlorine) is used in the succeeding operation of lixiviating, and frequently is not even sufficient for dissolving all the CuO and Cu_2Cl_2.

Lixiviation of the calcined mixture.—The mixture is carried in bogies running on tramways over each of the lixiviating tanks, and tipped into these. The only available material for the tanks is wood: most metals are excluded by the nature of the lixiviating liquid; stone, asphalt, &c. both by their costliness and by the heat of the charge. As such large wooden vessels cannot well be kept tight, on account of the unavoidably rough treatment and the hot acid lyes, the whole floor of the lixiviating shed is covered with a thick layer of asphalt, and slopes to one side, so that all liquors leaking out run off to a catch-well, into which enter at the same time earthenware spouts for carrying the strong copper-liquors.

The lixiviating tanks are square, about 11 × 11 feet wide and 4 to 5 feet deep, made of well-seasoned and planed 3-inch planks, kept together by corner-pieces, screw-bolts, &c. The joints are tightened by putting on a little red lead before putting the planks together; the bottom joints are besides caulked with tarred spun yarn, and the whole vessel painted with hot coal-tar. At Oker lead-lined vessels are used, which are very expensive and frequently needing repair. On the bottom, laths on end are placed; upon these, perforated fire-tiles or boards; upon this false bottom a layer of heather or coke (at Oker of straw) 3 to 6 inches deep is put. The liquors are conveyed in earthenware and india-rubber tubes of 3 to 4 inches diameter, the latter provided with iron pinch-clamps. In order to force the liquors from one tank to the other, or from the catch-well into the tanks, simple stoneware injectors are provided. Each tank has a steam-pipe for heating.

Into each tank about 10 tons of calcined ore are put, quite hot from the furnaces, and are first covered with weak liquor from a previous operation, which gets heated by the heat of the mass itself. After one or two hours the now concentrated liquor is run off by a plug-hole below the false bottom, and goes forward to the precipitation. The plug is put in again, and the lixiviation continued by hot water; thus weaker liquors are produced, which are forced to a fresh tank as just described. Generally three waters are put on, and thus most of the purest copper and 95 per cent. of all the silver contained in the pyrites are obtained. Then follow several (up to 6) washings with the weak condenser-acid, or, if this does not suffice, with muriatic acid bought for the purpose and much diluted. This is not necessary with mechanical furnaces, because the copper-salts from these are mostly soluble in water; but it is generally necessary with hand furnaces. Even when no acid need be bought, but sufficient condenser-acid is obtainable, a saving of acid is important, since the condenser-acid conveys arsenic and bismuth into the copper.

The liquors got by the use of acid contain many impurities, especially As, Bi, Sb, and Pb—according to Gibb, to 100 Cu, 5·4 As, and 0·3 Bi; and they are accordingly treated separately in most works, because they yield impure copper.

It is a principal rule to allow each water only to stand a few hours on the ore; the nine washings of each tank, together with charging and emptying it, are not to last beyond 48 hours. Accordingly, for each 5 tons of calcined ore obtained per diem one tank is required, and besides, on the whole, a few reserve tanks.

The residue from lixiviation, after draining, is tipped on a heap and afterwards sold to the iron-smelters. Just the value of this residue makes the wet process in this case more profitable than the dry process, as it forms a valuable iron-ore, going by the name of "purple ore" or "blue billy." The following is the composition of two average samples:—

Ferric oxide	90·61	95·10
Copper	0·15	0·18
Sulphur	0·08	0·07
Phosphorus	0	—
Lead sulphate	1·46	1·29
Calcium sulphate	0·37	0·49
Sodium sulphate	0·37	0·29
Sodium chloride	0·28	—
Insoluble	6·30	2·13
	99·62	99·55
Metallic iron	63·42	66·57

This ore is thus shown to be very rich in iron, entirely free from phosphorus, and to contain very little sulphur; its slight percentage of copper does no harm. The only drawback is its fine state of division. Attempts have been made, but unsuccessfully, to conglomerate it by means of lime for use in blast-furnaces (see above, p. 581); but success has been obtained in employing it directly in its pulverulent state as a mixture with 5 or even only 3 parts of lump iron-ore; using limestone in addition, both grey and white pig can be made from it. Most of this ore, however, is used for "fettling" the sides and bottom of puddling-furnaces in lieu of hæmatite, for which it is very well adapted. Its direct conversion into iron and steel on the large scale has not yet been carried out; but experiments in this direction made quite lately in America with the Du-Puy process ('Chemical News,' xxxix. p. 36) have been very successful. At Oker it is easily used up in the various metallurgical processes there carried on, and even its small percentage of copper is turned to account. They obtain, upon 100 parts of pyrites-cinders, 75 parts of extraction residues of the following composition:—

Ferric oxide	79 per cent.
Alumina	3 „
Magnesia and alkalies	1 „
Lime	2·5 „
Sulphuric acid	5·5 „
Insoluble in acids	6 „

The purple ore is the more valued the freer it is from siliceous gangue; and for this reason that made from Spanish and Portuguese is preferred to that from Norwegian pyrites.

the purple ore is employed for preparing the latter.

The effect of the lixiviation is best seen from the following analyses by Gibb, which at the same time illustrate the great difference of work between mechanical and hand-worked furnaces :—

	Mechanical-Furnace Ore.		Hand-worked-Furnace Ore.	
	per cent.	Copper, per cent.	per cent.	Copper, per cent.
Soluble in Water :—				
Cupric chloride	4·16	1·96	3·81	1·82
Cuprous chloride	none		·19	·12
Cupric sulphate	1·83	·81	none	
Ferrous sulphate	·15		none	
Ferric sulphate	·75		none	
Zinc sulphate	2·01		1·95	
Calcium sulphate	1·29		1·39	
Sodium sulphate	9·17		11·13	
Sodium chloride	none		2·64	
Soluble in dilute Hydrochloric Acid :—				
Cuprous chloride	·015	·01	·33	·21
Cupric oxide	·225	·18	1·01	·81
Lead sulphate Ferric oxide	not determined.		not determined.	
Residue (by difference) :—				
"Purple iron ore"	80·40	·08	77·55	·11
	100·00	3·04	100·00	3·07
Sodium chloride equivalent to sodium salts as above	7·56		11·81	

The composition of the copper-liquor, according to Gibb, is, in grams per litre :—

	From hand-work Furnaces.		From mechanical Furnaces.
Sodium sulphate	144·1	Sodium sulphate	110·9
Sodium chloride	63·9	Sodium chloride	4·1
Chlorine in combination with heavy metals	67·1		
Copper	53·0	Cuprous chloride	53·2
		Cupric chloride	0·8
Zinc	6·9	Zinc sulphate	10·1
Lead	0·6	Lead sulphate	0·8
Iron	0·5	Ferrous sulphate	4·3
Calcium	0·7	Calcium sulphate	5·0
Silver	0·047	Silver	not estimated.

At Oker the process is carried out in the following way. The calcined charge is lixiviated in parcels of 5 tons each, first with the "final liquor," which is always regenerated in the process. 100 parts of the latter, of 1·145 spec. grav., contained :—

	per cent.		per cent.
Cu	0·015	CoO+NiO...	0·01
Pb	trace	CaO	0·12
FeO	2·14	MgO	0·52
Fe_2O_3	0·15	Alkalies	2·61
Al_2O_3	0·11	Cl	2·56
ZnO	0·06	SO_3............	5·89
MnO	0·31	As+Sb	trace

Total solids...... 14·495 per cent.

This liquor, already heated in pumping by the injector to 50° C., is further heated, when it comes into contact with the calcined charge, by the solution of the anhydrous salts, of course also by the heat of the charge itself, nearly up to the boiling-point, by which the solution is assisted. When the charge is perfectly penetrated by the final liquor, the outlet-tap is opened and fresh final liquor runs in as long as the copper-liquor running away at the bottom still shows a blue colour. This first period lasts four or five hours, and furnishes a copper-liquor of 1·355 spec. grav., and of the following composition :—

	per cent.		per cent.
Cu	3·71	CoO+Nio ...	0·04
Pb	0·01	CaO	trace
Ag	0·005	MgO	0·27
Bi	trace	Alkalies	10·60
$Fe_2O_3+Al_2O_3$.	0·29	Cl	12·56
ZnO	4·97	SO_3...........	8·95
MnO	0·58	As+Sb	0·32

Total solids......... 42·305 per cent.

After the first lixiviation is over, the dilute condenser-acid, first brought to boiling, is run into the tanks and allowed to act for twenty-four hours; then it is run off, and a third lixiviation effected by dilute sulphuric acid. For 5 tons of ore 2½ cwt. of boiling-point, is employed, and allowed to remain in contact with the ore for two days, or until the liquor acquires a neutral reaction. Its analysis showed :—

	per cent.		per cent.
Cu	0·58	CaO	0·07
$Al_2O_3 + Fe_2O_3$	2·13	MgO	0·04
ZnO	0·06	Alkalies	0·62
MnO	0·12	Cl	0·13
Co + Ni	0·02	SO_3	2·39

Total solids ...... 6·160 per cent.

The first copper-liquors contain most of the silver, and are therefore kept apart from the later liquors, poorer in this respect.

The cupric chloride is, of course, easily dissolved in the final liquor; the cuprous chloride in the presence of alkaline chlorides is also dissolved at a higher temperature without difficulty; lastly, cupric oxide is to be converted into $CuCl_2$ and Cu_2Cl_2 by the $FeCl_2$ of the final liquor, and to become soluble thereby ($2FeCl_2 + 3CuO = Fe_2O_3 + Cu_2Cl_2 + CuCl_2$); but this could only be done by an intimate mechanical mixture of the liquor with the ore; and it is therefore preferred to dissolve merely 75 to 80 per cent. of the copper by means of the final liquor, and the remainder by further lixiviations with dilute acids. In Bräuning's paper no hint is given in what way the increase of impurities in the final liquor is prevented. No doubt only a portion of it is taken back into use, and another portion run to waste; so that there must always be a partial renewal.

Precipitation of the Copper from the Liquors.

This is sometimes preceded by a special treatment for obtaining the silver, which will be described afterwards. The precipitation of the copper now takes place everywhere by means of metallic iron, since the ingenious process of Gibb has been given up again. The latter consisted in precipitating the copper by sulphuretted hydrogen, which was recovered at a later stage of the process; the precipitated cupric sulphide was washed and pressed in a filter-press, and smelted in furnaces in the usual way into "coarse metal." The acid mother-liquors containing the whole of the sodium sulphate were evaporated to dryness in a furnace, mixed with small coal and reduced in another furnace; thus a mass containing nearly 35 per cent. of sodium sulphide and 2·4 per cent. of sodium carbonate was obtained. This was lixiviated with hot water; the solution was systematically treated with impure carbonic acid, obtained by burning coke; and thus on the one hand sulphuretted hydrogen was given off, which served for precipitating the copper in the first stage of the process; on the other hand a solution of sodium carbonate was obtained, which, after evaporation and calcination, went into the trade as soda-ash. But this process was only applicable to the liquors obtained from the mechanical calcining-furnace (that is, with a minimum addition of common salt); for in the liquors from the ordinary hand-worked furnaces there would be 1 part of NaCl to each 4 parts of Na_2SO_4, which would furnish a very weak soda-ash. This very ingenious process was worked out in all its details, and practically carried out on a very large scale, at the Bede metal-works; but it has been given up again, partly because the carbonic acid was too dear, and partly because no furnace-bottom could be constructed fit for resisting the acid liquors for any length of time—partly also because the quality of the soda-ash was too unequal—and finally because the copper was only obtained as sulphide, and had to be smelted at a greater expense than that precipitated by iron.

For this latter process either scrap wrought iron, or scrap cast metal, or "spongy iron" reduced from the residue is employed. Apart from the latter, the thinnest scrap is the best, such as the hoops of cotton or esparto bales; but as light scrap is generally rather dirtier than heavy scrap, the copper from the former is rather more impure than that from the latter. The precipitation takes place in wooden tanks exactly of the same kind as those used for lixiviation, and furnished with a steam-pipe. They are filled with scrap-iron; copper-liquor is run upon it, and steam is turned on; the heating is continued till a bright strip of iron, held in the liquid, no longer indicates the presence of copper in solution. At Oker, according to the degree of concentration of the liquors, the boiling takes place twice or three times before all the copper is thrown down; the process lasts from one to three days, and requires as much iron as the weight of copper produced, which proves that a large portion of the latter must have been in solution as Cu_2Cl_2. Once a month the precipitated copper is removed from the tanks and washed.

After precipitation, at some works the liquor is passed through a hair sieve in order to separate the copper present in a fine state of division; the copper is washed off the residual iron by a jet of water, or a besom, &c., and left to settle in special tanks. At other works a less rough arrangement is in use, viz. round tubs with wooden agitators, an annular place being fenced off in their upper part for the scrap iron. The agitation of the liquid causes each part of it to come into contact with the scrap iron much more quickly, so that the liquids are much sooner freed from copper than in the process first described; besides, the precipitated copper is at once washed off the iron and carried along with the exhausted liquor into settlers, and the process in the precipitating-tubs started again at once, after adding a little more iron.

A continuously acting apparatus for the precipitation of copper has been constructed by Hauch (Dingler's Journal, ccxxiii. p. 286). It consists of a cask revolving round a horizontal axis, provided with ledges inside and filled with iron borings; copper-liquor is let in, and is speedily exhausted by the rotation of the cask, the copper being at the same time washed off the iron. By combining several casks and systematically allowing the liquor to run into that cask which has been working the longest time, it is possible to obtain a continuous supply of fresh copper-liquor and a continuous running-off of exhausted liquor holding the copper in suspension. Another continuous copper-precipitating apparatus has been described by Kerpely (Wagner's Jahresb. 1877, p. 165).

The precipitation takes place most quickly by employing "*spongy iron*," as is done at the Bede metal-works. This product is made by reducing ferric oxide at so low a temperature that the iron cannot combine with carbon and cannot melt, but remains in the finely divided state, as a "sponge." This method (which may probably play an important part in the metallurgy of iron and steel, if C.W. Siemens's or Du Puy's experiments lead to a successful issue) was tried in England for the first time in 1837. Bronac and Deherrypon used it in 1859 for the precipitation of copper, but only in the dry way; but Gossage in the same year introduced the spongy iron in the wet method of copper-extraction. Further patents upon this matter were taken out by Aas in 1861 and by Bischof in 1862.

Several furnaces have been proposed for this purpose; but only one of them is in use. This is a reverberatory furnace in which the flame, after having passed directly over the charge, returns below the

Fig. 303.

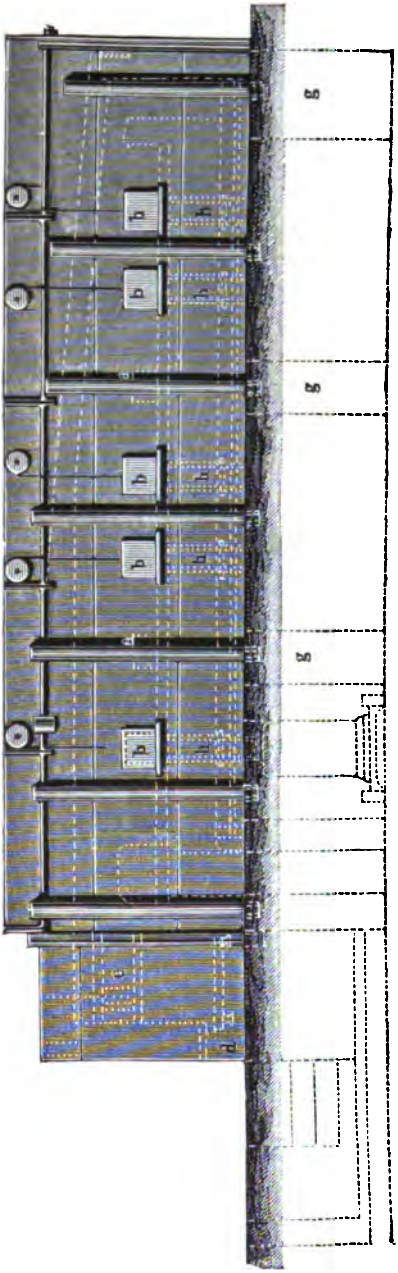
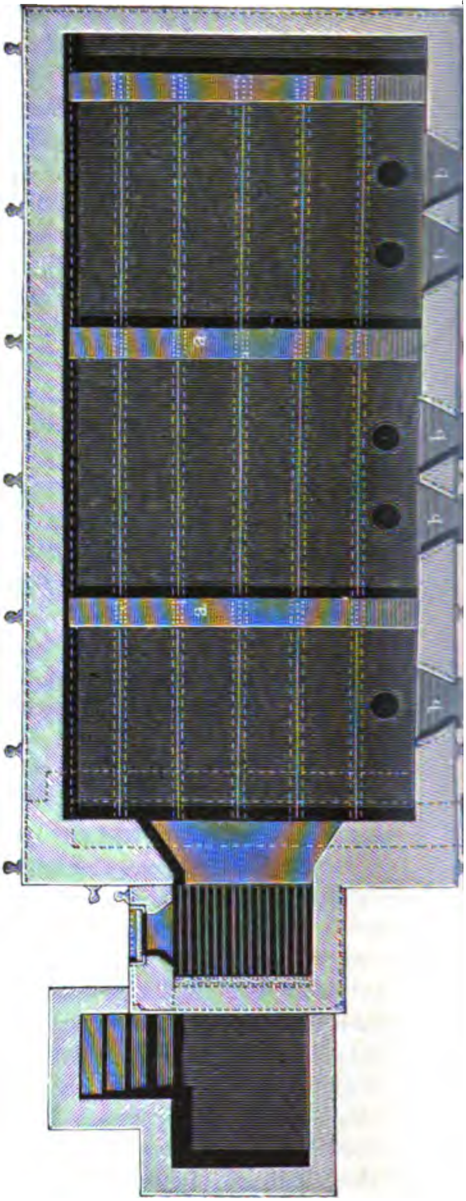
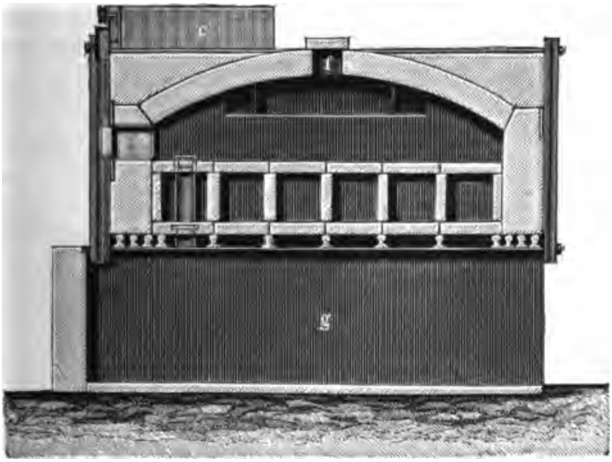


Fig. 304.



furnace-bed, and thus heats the charge indirectly from below. Figs. 303 to 305 show all the essential details of the furnace. It is, in the drawing, 28 feet 9 inches long; the working-bed has a length of 22 or 23 feet and a width of 8 feet. Dwarf walls, *a a*, 9 inches high, divide it into three compartments, which on one side have two working-doors, *b b*, each. Each compartment is charged and finished by itself. The working-doors are of cast metal, and run air-tight in frames; the same is the case with the fire-door. The fire-place is constructed for generating a reducing flame; the grate has a surface of 4 × 3 feet; and the bearers, *d*, are 3 feet, latterly even 4 feet 8 inches below the fire-bridge; so that a very deep layer of fuel is obtained, which does not allow any oxygen to get inside the furnace. The furnace-bed is formed by fire-tiles 4 inches thick, with rabbeted edges, partly resting upon the walls forming the divisions of the lower flues, partly upon railway-bars. The flame having travelled through these flues, descends in a vertical shaft along the fire-bridge, and thence goes to the chimney. In this descending shaft there is a fireclay damper, which is closed every time before a working-door or fire-door is opened. The 9-inch furnace-roof is surmounted by a flat cast-iron dish, *e*, supported by short pillars, for drying the ore and mixing it with coal; the mixture is charged into the furnace through the 6-inch pipes *f*

Fig. 305.



coals on the grate, care being taken that the burning mass does not become hollow, lest uncombined oxygen should get inside the furnace. The time of reduction in the compartment nearest the fire-bridge varies from 9 to 12 hours; in the second it is about 18 hours, in the third about 24 hours. The depth of the charge lying on the bed is about 6 inches. During the time of reduction each compartment must be turned over twice, or even three times. Although during this time the damper is closed, a little air always enters the furnace; but the turning-over is indispensable, as the mass would otherwise cake together. The time above stated refers to a bright red heat; a low red heat is sufficient for reduction; and the iron thus made is even better for the precipitation of copper; but as in this case much more time is required for reduction (up to 60 hours), this style of working doos not pay. The fireplace being so deep, fresh coal need only be thrown in twice or three times every twelve hours, say 15 cwt. for a ton of ore.

The completion of the reduction is ascertained by testing. A small sample is taken out, put on an iron plate, covered with a brick till it has become cold, and 1 gram of the (unoxidized) central part tested by a cupric sulphate solution of known strength, which is run from a burette onto the spongy iron with frequent stirring; from time to time a drop is put on a bright blade of iron, to see whether any stain of copper is produced upon it. When the reaction in any of the three compartments is finished, the damper is closed; two of the discharging-boxes are run underneath the furnace, and their mouths connected with the discharging-pipes by an iron hoop luted with clay; then the charge is raked down into the boxes as quickly as possible. The boxes are then closed with the loose cover, run out again, and allowed to cool for forty-eight hours. They are then lifted by a crane, and the cotters are knocked out; whereupon the bottom turns upon its hinges and the whole mass of spongy iron readily falls out, owing to the box tapering upwards. The sponge is then finely ground by a heavy edge-runner 6 feet in diameter, and passed through a sieve with fifty holes per linear inch; it is now ready for the precipitation of copper.

Two different materials have been proposed for preparing spongy iron, viz. pyrites-cinders direct from the chemical works, and the "purple ore" of the copper-works themselves. The following difference between them :—

	Pyrites-cinders. per cent.	Purple ore. per cent.
Ferric oxide	78·15	95·10
Iron	3·76	......
Copper	1·55	0·18
Sulphur	3·62	0·07
Cupric oxide	2·70	......
Zinc oxide	0·47	......
Lead oxide	0·84	0·96
Calcium oxide	0·28	0·20
Sodium oxide	......	0·13
Sulphur trioxide	5·80	0·78
Arsenic pentoxide	0·25	......
Siliceous residue	1·85	2·13
	99·27	99·55

Both Bischof and Gossage proposed the direct use of burnt ore for preparing spongy iron, from the apparent advantage of utilizing its copper without the trouble of wet extraction. Unfortunately, however, the arsenic contained in the burnt ore remains in the spongy iron, gets into the copper, and greatly injures its quality. G. Bischof, to be sure, in his patent of 1862, asserts that arsenic and lead volatilize; Gibb, however, admits this to be the case only for the lead to a great extent, whilst arsenic, being present mostly as arseniates of iron and copper, soon forms stable arseniurets. In fact the spongy iron made direct from pyrites-cinders contains nearly as much arsenic as was originally present in the cinders. On the other hand, the purple ore only retains faint traces of arsenic; it is therefore exclusively used for spongy iron now. The following is an analysis of the spongy iron made in the above way :—

Ferric oxide	8·15	per cent.
Ferrous oxide	2·40	„
Metallic iron	70·40	„
Copper	0·24	„
Lead	0·27	„
Carbon	7·60	„

Alumina	0·19	„
Zinc	0·30	„
Siliceous residue	9·00	„
	99·62	

When spongy iron is employed for the precipitation of copper, continuous stirring is required, for which at some works mechanical agitators are used, at others manual labour; at the Bede metal-works an india-rubber hose, through which a blast of air passes, is moved about in the tank. A Körting's blower would, no doubt, be the best apparatus for this purpose. Perfect mixture is thus obtained; and the precipitated copper only contains 1 per cent. metallic iron, with a great saving of space, apparatus, and labour, as against the work with scrap-iron. However, the greater cheapness of material and treatment in employing spongy iron is bought at the expense of a greater contamination of the copper by unreduced iron oxides and carbon; at the majority of works, therefore, scrap-iron is still preferred. This, of course, depends also on the local price of the latter.

According to Bischof, with spongy iron the arsenic is only precipitated after a few hours, long after the copper has been precipitated, which thus remains free from arsenic. Gibb, however, from many years' experience on the large scale, states that he never found any trace of arsenic in solution after the copper had been precipitated, whichever form of iron or solution of copper might be employed.

The composition of the copper precipitated by the various methods is shown by the following analyses (by Gibb) :—

	Precipitated by		
	Spongy Iron.	Heavy Scrap.	Light Scrap.
	per cent.	per cent.	per cent.
Copper	67·50	72·50	67·50
Arsenic	·137	·306	·100
Silver	·011	·046	·066
Lead	1·30	2·60	1·74
Ferric oxide	5·15	4·41	7·56
Carbon	5·10		
Silica	3·20		

At Oker the composition of the copper precipitated by scrap-iron and dried at 100° C. was:—

Cu	77·45	per cent.
Pb	0·63	„
Ag	0·10	„
Bi	0·006	„
As	0·04	„
Sb	0·15	„
Fe_2O_3	6·72	„
Al_2O_3	0·99	„
Zn	1·02	„
Mn	0·02	„
Co + Ni	0·03	„
CaO	0·10	„
MgO + Alkalies	2·71	„
SO_3	4·58	„
Cl	1·19	„
Insoluble in acids	0·61	„
Oxygen + moisture (by loss)	3·654	„
	100·000	

This product is either sent to copper-smelting works or smelted at the wet-extraction works themselves. The copper precipitated from the aqueous solutions, if kept separate from that from the acid solutions, can always be smelted directly for blister copper by adding to it lime and slags; the copper from the acid solutions is frequently so impure that it has to be mixed with raw ore, or else with soda-waste and slags, and smelted for "coarse metal," which yields blister copper only after a second roasting. Finally the usual refining takes place. At other works both precipitates are melted together, being charged at once into the furnace in the moist state. The slags produced in this operation, containing from 3 to 10 per cent. of copper, are utilized by smelting them for coarse metal (in a round blast-furnace, 3 feet wide, with four tuyeres), with the addition of soda-waste (calcium sulphide and carbonate). The mass collects in a well, where the coarse metal separates from the slag, and the slag (a "singulosilicate") continually runs off into a bogie. In order that such furnaces may be quickly taken down when the separated iron renders the smelting difficult or impossible, the upper furnace-shaft, together with its jacket, is supported on iron pillars, so that the proper smelting-shaft up to a height of 5 or 6 feet stands quite free within the pillars. The coarse metal here obtained contains about 30 per cent. of copper, and is worked up in the usual way by calcining, smelting, and roasting.

The *furnaces for smelting the copper precipitate* used at English wet-extraction works are reverberatory furnaces of the well-known Swansea type. After smelting, the slag is skimmed off, and the copper tapped as blister. When spongy iron has been used, the excess of carbon prevents the copper from being melted directly to blister; therefore about one half of the precipitate is calcined in large calciners similar to those for calcining burnt ores with salt. Here the carbon is burnt off, and the copper partly oxidized; the calcined precipitate is mixed with raw precipitate and smelted, as above, for blister. The blister copper is refined by roasting to oxidize the iron, sulphur, &c., followed by reducing by charcoal the oxide of copper produced in the roasting, and poling according to the method usually employed by the copper-smelter.

The copper produced is pure and tough. It takes a good place as a marketable article; and its composition in comparison, with that of English copper made by the ordinary method of smelting may be judged from the following analyses :—

	Copper from Wet Process.		"English" Copper, Field's Analyses.	
			B.S.	Tough.
	per cent.	per cent.	per cent.	per cent.
Silver	·022	·016	·035	·047
Arsenic	·030	·170	·105	·090
Antimony	none.	trace.	·010	trace.
Bismuth	·006	·019	·035	·130
Lead	none.	·002	none.	—

The complete removal of the arsenic is said to be effected, according to a patent of Bischof's (in 1862), by precipitation with spongy iron—according to a patent of Down's (1870), by almost completely neutralizing the copper-liquors with lime, followed by precipitation with scrap iron; the foreign metals are said to remain in solution in this case (?). Gibb declares both statements to be entirely erroneous (comp. above, p. 620); but it is quite possible that in Down's process the arsenic is removed at a previous stage, viz. on neutralizing, as ferric arseniate.

On laying out a copper-extraction works the levels must be carefully attended to, so that the very large quantities of solid substances and liquors may be easily moved about. At Oker, Hebburn, &c. all the apparatus are arranged at different levels. The design of the Oker works has been published by Bräuning (*l. c.*). The top level is occupied by the charging-loft, to which the burnt ore and the salt are brought by bogies; attached to it are two edge-runners, each of which grinds daily 15 tons of ore and 2¼ tons of salt down to a size of 2 millims. The mixture is taken by bogies to the furnaces, situated at a little lower level; the furnaces are heated by gas-producers, situated lower down again. Below the furnaces there follow, at three descending levels, the lixiviating tanks, the precipitation-tanks, and cisterns for the "final liquor," from which it is pumped up again by injectors and used for lixiviating fresh ores.

Utilization of the sodium sulphate contained in the mother-liquors from the precipitation of copper.—We have mentioned above the process of Gibb and Gelstharpe (p. 613), which has been given up again. At present the acid mother-liquors are everywhere let run into the rivers, and the sodium sulphate contained in them is lost. At a large copper-works for a time a process was employed by which ferric oxide was simultaneously obtained of great purity and fineness, so that it could be sold on the large scale for red paint. The acid liquors were boiled down to dryness in a brick furnace; the residual mass of sodium sulphate and chloride and iron salts was ignited, and ground very fine under edge-rollers; it was then carefully calcined in an ordinary calciner until all the iron salts were peroxidized. The mass was treated with hot water and allowed to settle; the ferric oxide deposited only required washing in order to become marketable as Venetian red. The solution (containing chiefly Na_2SO_4 and NaCl) was concentrated in pans by means of steam circulating in a worm, an agitator preventing the salt from adhering in crusts to the bottom and sides of the pan and to the worm. At a concentration of 1·37 to 1·40 sp. grav. nearly all the sulphate was found to be separated; the liquor with the suspended salt was drained off the precipitate, which was washed with a little hot water and dried in a furnace. It contained only about ¼ per cent. of NaCl, and not a trace of iron; so that it was very well adapted for glass-making. The high price of coals caused this process to be given up at the time; and it does not seem to have been taken up again. Probably the first step, viz. the evaporation of the acid liquors in a brick furnace, would present the same difficulties as in Gibb's process.

Treatment for obtaining the Silver.—According to Phillips, the cupreous pyrites-cinders contain on the average 0·0027 per cent. Ag and 0·0001 per cent. Au. These metals on calcining with salt are converted into chlorides; and, owing to the solubility of AgCl in NaCl, the silver is found mostly, the gold at least partly, in the liquors obtained by lixiviating the calcined ore. In order to further this, Phillips adds some more common salt in the lixiviating tanks. These metals are only recovered in a few works, either by the process of Claudet (1871) or that of Gibb (1873). The former, which is carried out at Widnes and elsewhere, consists in precipitating by a soluble iodide the silver from the liquors in the state of AgI, which is quite insoluble in solutions of chlorides. Only the first three liquors (which contain 95 per cent. of all the silver) are employed; the diluted state of the other liquors would make the recovery of the silver from them unprofitable. The liquors, before they undergo precipitation with iron, are completely settled, run into a gauged tank, and their contents of silver accurately estimated by adding to a certain volume muriatic acid and a solution of lead acetate, and afterwards potassium iodide. The precipitate is collected on a filter, washed, dried, and fused with a flux of soda, borax, and the finest carbon. The lead regulus obtained is cupellated; and from the weight of the silver thus obtained, that contained in the liquors is computed. To the liquor a solution of potassium or zinc iodide of known strength is now added in sufficient quantity to precipitate all the silver; the iodide solution is diluted to such an extent that it amounts to about $\frac{1}{10}$ the volume of the liquid; the precipitate is allowed to settle; the clear liquor is tested in the laboratory to see if all the silver is thrown down; and if so, it is run into the tanks for precipitating the copper, where it is treated in the usual way. The quantity of iodide employed for the precipitation is much larger than that corresponding to the silver present, since a portion of the lead is thrown down as PbI_2. Probably the silver is precipitated before the lead; but as it is not with the iodide before the latter has also come into contact with molecules of lead, the precipitate always contains a good deal of lead; so that necessarily a corresponding excess of the precipitant is required.

The precipitate, consisting mainly of AgI, PbI_2, and $PbSO_4$ (which falls down on the liquor cooling), is well washed with water; and if a sufficient quantity of it has been collected, it is treated in the moist state and hot with metallic zinc and a little muriatic acid. Thus the AgI and PbI_2 are decomposed completely, the $PbSO_4$ partly, and a liquor containing *zinc iodide* is obtained, which is employed over again for precipitating argentiferous liquors in proportion to its percentage of iodine. On the other hand, a metallic sponge, mixed with pieces of zinc, is obtained having the following composition:—

Ag	5·95
Au	0·06
Pb	62·28
Cu	0·60
ZnO	15·46
Fe_2O_3	1·50
CaO	1·10
SO_3	7·68
Insoluble residue	1·75
Oxygen and loss	3·62
	100·00

This is sent to the silver-works. Usually the argentiferous copper-liquor is first mixed with the solution of ZnI_2 obtained in reducing the AgI &c., and the last portion of the silver precipitated by KI. A certain loss of the latter is unavoidable, whatever care be taken. In this way Phillips obtains about two thirds of the total silver contained in the burnt ore, and about a similar proportion of the gold; several others have not been content with this, and have given up the process, probably because sometimes on calcining with salt too much Cu_2Cl_2 is formed (its quantity varies from 0 upon 6·70 $CuCl_2$ to 0·62 Cu_2Cl_2 upon 3·75 $CuCl_2$), and in its presence the silver seems to be incompletely precipitated by iodides. At avoid the formation of cupreous chloride; and, perhaps just from this cause, Claudet's process has been more successful there than elsewhere.

An important improvement on Claudet's process, if it should turn out a success, would be the process of E. L. Mayer, patented in 1877. The copper-liquor is to be precipitated with a solution of glue and KI; the solution may contain very much copper and only a few thousandths per cent. of Ag. After the precipitate has settled down, a solution of tannin is added and a little more precipitate obtained. The precipitates are washed with similar dilute acid as serves for dissolving the copper-ores in order to remove the copper they may contain. The acid is neutralized with lime, and treated with alkaline sulphides in a revolving drum till all iodine is removed; the solution containing iodides can be used for again precipitating silver. The remaining sulphides of lead, silver, &c. are to be worked for silver. The addition of glue and afterwards of tannin has for its object to conglomerate the extremely finely divided AgI (of which otherwise a portion would escape collection) into a larger mass.

Gibb's process is based on the observation, made by him, that if a copper solution containing very little silver is treated with sulphuretted hydrogen, by far the largest portion of the silver is thrown down as Ag_2S with the first portions of CuS. The H_2S is made from the tank-waste of alkali-works by treatment with dilute hydrochloric acid in wooden vessels; the hydrochloric acid enters the vessel underneath a false bottom made of boards covered with furnace-slags, and runs out near the top completely saturated. The vessels need not be air-tight, as the gas is aspirated from them by an air-pump, the delivery-pipe of which is provided with branches for every one of the precipitating-tanks; an india-rubber hose conveys the gas into these, and, when moved about in the liquid, sufficiently agitates it by the escaping gas. The process is continued when as nearly as possible 6 per cent. of the copper has been precipitated, which generally takes 20 minutes. The bulk of the copper, which otherwise shows on the average 18 ounces of silver per ton, shows after this treatment only 2 to 4 ounces. The 6-per-cent. CuS precipitated at first, however, contains 200 ounces silver per ton. The dilution of the gas by air seems to be favourable to the process. The precipitate is allowed to separate into clear liquor and denser mud; it is washed several times by decantation, and then pressed in a Needham's filter-press. The damp sulphides are calcined in an ordinary calciner; the product contains one fourth of the copper as sulphate, the remainder as oxide or oxychloride, and the silver altogether as chloride. It is roughly ground, washed with water, and the solution of $CuSO_4$, which only contains 1 ounce of silver to the ton of copper, precipitated as usual. The residue, mostly CuO, is systematically extracted by hot concentrated solution of common salt, which dissolves nearly all the silver, leaving only 3 to 4 ounces of silver per ton of copper in the residue. The solution containing the silver is precipitated by milk of lime, the precipitate washed with water to remove the $CaCl_2$, then with dilute sulphuric acid to dissolve the copper, then again with water, and leaves at last a residue containing 9 per cent. of silver as AgCl, worth £700 per ton. It contains besides principally the sulphates of calcium and lead. This treatment is said to cost 9*d.* per ton of burnt ore, and to yield about ½ ounce of silver, of the value of 2*s.* 6*d.*; but, in this shape, it appears to have been given up again.

Chadwick and Jardine, in 1875, patented a new desilverizing process, which is said to be in use at Henderson's works at Irvine. The copper-liquors are diluted to 20° or 25° Tw., and a very weak solution of lead acetate added, which is equivalent to the whole of the Ag, As, Sb, and Bi, less any Pb already contained in the pyrites. Usually about 230 grams of brown sugar of lead per ton is used. On agitating, a light-yellow precipitate is obtained, consisting of 53 per cent. lead sulphate, 5–6 per cent. silver sulphate, and 3 ounces of gold per ton of precipitate (say, 0·01 per cent.). After thorough washing, the gold and silver can be obtained by smelting and refining in the usual way. The copper is said to be thus obtained free from As, Sb, and Bi.

According to a patent of Snelus (1875), finely divided iron dust is to be injected by a blower into the copper-liquors, just sufficient to precipitate 19 per cent. of all the copper; this is said to carry down 80 per cent. of all the silver contained in the solution.

A new patent by Phillips (No. 3923, Oct. 10th, 1877) prescribes mixing the copper precipitate with common salt and soda, moistening with water, and grinding in a pug-mill to a paste. The mass is dried and calcined in a reverberatory furnace, constantly stirring, till all the copper has been converted into CuO and all the silver into AgCl. The alkali added decomposes any volatile copper salt present, and almost entirely prevents any volatilization of silver calcined mass by treatment with a hot solution of common salt. (This is essentially like Augustin's process of 1840, applied to the extraction of silver from ordinary ores.)

According to Hunt's 'Mineral Statistics' for 1874, p. 65, there existed in Great Britain in that year 22 copper-works for wet-extraction, which together consumed 329,000 tons of burnt ores (say, equal to 450,000 tons of pyrites). Two of them made blue copperas; three went as far as refined copper; the others sold their precipitate to copper-smelting works. The total production of copper from this source in 1874 amounted to 9000 tons.

Another process of extracting copper from pyrites-cinders has been described by Jetzler ('Dingler's Journal,' ccxvii. p. 478). He worked pyrites from Borsa-Bánya, in Hungary, containing only 1·01 Cu. The burnt ore decays easily on lying in the air; and after sifting off the not decayed core through a sieve with 10 meshes to 1 centim. square, the copper can be extracted by hot weak muriatic acid of 3°–4° Tw.; probably Fe_2Cl_6 acts here, chlorinating the lower sulphides of copper, and being reduced to $FeCl_2$. On washing, solutions of 24° Tw. are obtained, which, besides copper, contain Ag, Pb, $Al_2(SO_4)_3$, &c. The metals were precipitated by scrap iron; and the precipitate was sold to a smelting-works according to its value of Cu and Ag. The process did not pay very well, as the residue could not be used as an iron-ore.

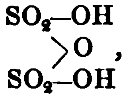
Another process has been patented (in 1873) to Baron Leithner in Austria ('Dingler's Journal,' ccxi. p. 349). The burnt ore (in this case containing about 1 per cent. of copper) is to be smelted with 36 per cent. calcium hydrate in a kiln heated by the waste gas of a blast-furnace; the product is to be smelted for pig-iron, which now contains 2·09 per cent. Cu; and this is to be used for precipitating copper; so that its own copper is utilized as well.

Some new patents of Mason's (Nos. 2984, 2992, and 2993, 1877) seem to contain nothing of any importance that is new.

The whole of the processes connected with the wet extraction of copper, as far as published up to the end of 1878, and including many proposals or actually employed processes not mentioned here (because they do not refer specially to the treatment of pyrites-cinders from sulphuric-acid works), are described in a condensed form by Bode (Dingler's Journal, ccxxxi. pp. 254, 357, 428).

CHAPTER XVII.

THE MANUFACTURE OF NORDHAUSEN OR FUMING OIL OF VITRIOL, AND OF SULPHURIC ANHYDRIDE.

Already in the first Chapter the fuming oil of vitriol has been described, and has been characterized as a mixture of sulphuric hydrate and pyrosulphuric acid,  $\left.\begin{matrix}SO_2\text{—}OH\\ SO_2\text{—}OH\end{matrix}\right\rangle O$, a compound which latterly has come into the market as "solid oil of vitriol."

Although in all probability the fuming oil of vitriol is precisely that kind of sulphuric acid which was obtained first of all, and although a generation ago it was manufactured in several places, and especially near Nordhausen, in Prussian Saxony, latterly its manufacture according to the only method formerly employed has been carried on exclusively in Bohemia, by the firm of Johann David Starck. The reason of this was that in this manufacture manual labour constitutes a very large portion of the expense, and that it requires a very large space and a great number of small apparatus, so that it can only pay under certain conditions rarely present. Owing to this, all other factories have ceased to work, even those in the Harz (which, by the way, were not located at Nordhausen itself, where there was only a warehouse for the acid, but at Braunlage and Goslar).

So long as fuming oil of vitriol was only used for dissolving indigo, the monopoly of the Bohemian firm was not very much felt; but since very large quantities of fuming acid are required for refining ozokerite and especially in the manufacture of alizarine and eosine, many efforts have been made at producing that acid in another way; and success has at last been attained. The attempt has been cannot be replaced by other sulphates yielding their acid on heating, partly or entirely as anhydride; and, secondly, trying whether the anhydride (as a solution of which in sulphuric hydrate the "oleum" can be viewed) cannot be obtained synthetically.

These methods shall be mentioned later on; we must, however, in the first place describe the method by which the oil of vitriol was exclusively supplied up to nearly the present time—namely, from "vitriol stone"—which rests on the fact that ferric sulphate, $Fe_2(SO_4)_3$, at a red heat splits up into ferric oxide (Fe_2O_3) and sulphuric anhydride ($3SO_3$), the latter of which is partly decomposed into SO_2 and O.

The manufacture of fuming oil of vitriol from "vitriol stone."

All former descriptions of this manufacture have been made obsolete by that given by E. V. Jahn in Wagner's 'Jahresbericht,' 1873, p. 220. We shall give an abstract of the latter, adding some supplementary notes.

The basis of the whole manufacture is constituted by the Przibram slates, belonging to the Silurian formation and lying directly over the palæozoic clay-slate. They are of different kinds: either they are quite similar to the palæozoic clay-slates and can be partly used as roofing-slates (these are called "dead slates"), or they contain coal and from 1 to 31 per cent. of pyrites. The latter can be readily distinguished by their darker colour and considerable specific gravity; they are called "alum-slates," or, more appropriately, "copperas-slates." They occur in large seams, up to 20 fathoms thick, at the edge of the Pilsen-Wald beds; they are most frequently met with at the banks of watercourses, where the water has denuded the surface, and are distinguished by their oxidability and frequent efflorescence of copperas. Sometimes their influence, where they have been confounded with the less-decaying slates in erecting railway embankments &c., is felt in a very unpleasant way. The oxidability of the copperas-slates has led to a special industry, which has existed since the 16th century. When rich in aluminium (which is only exceptional), the slates serve for making alum; when poor in alumina and rich in pyrites, for copperas and "vitriol stone" (*Vitriolstein*), *i. e.* ferric sulphate—from which naturally followed the manufacture of fuming oil of vitriol. The Pilsen sulphur-works are already mentioned in 1526; the fuming oil of vitriol is the oldest form of sulphuric acid, and was first manufactured in Bohemia, whence it was driven by the horrors of the thirty years' war and the following horrors of the counter-reformation; and the Nordhausen country received it. For some time past, however, that industry, having ceased to exist near Nordhausen, has returned to its old home in Bohemia, where it was favoured by the presence of large stores of fossil fuel in the immediate vicinity of the copperas-slates. Since 1778, at Gross-Lukavic, the manufacture of oleum has been resumed, but only since 1792 on a larger scale, when Johann David Starck took it in hand, at first with the assistance of men obtained from the Nordhausen factories. He first used calcined copperas, then "vitriol stone" bought at Altsattel. He also made larger quantities of ordinary sulphuric acid, and advanced the whole industrial development of that country to such an extent that in 1836 he was ennobled. The firm is still carried on by his son, who has all but monopolized the manufacture of fuming acid, which, however, is only one of the branches of his enormous establishments, yearly putting into the market goods to the value of nearly half a million sterling. The principal seats of the manufacture of fuming vitriol are at Bras, Kasnau, Bykov, and Davidsthal. It consists of three branches:—1st, the production of the vitriol stone; 2nd, the distillation of "oleum;" 3rd, the production of "caput mortuum."

The production of vitriol stone originally took place from the mother-liquors of copperas- and alum-making, which principally contain ferric sulphate; but it now comes chiefly from the copperas-slate ("Vitriolschiefer"), of which Anthon has given the following analyses:—

	From Weissgrün.				
	I.	II.	Darova.	Hromic.	Briza.
Souble in water:—					
Sulphates of Ca, Mg, Fe	1·20	2·80	1·00	1·60	0·80
Insoluble:—					
Iron sulphide	12·37	31·53	14·50	11·58	14·33
Ferric oxide	0·76	2·17	2·42	0·16	0·64
Alumina	3·50	2·40	2·80	1·20	1·30
Silica	74·90	55·96	71·21	75·70	73·40
Carbon	6·09	4·99	6·84	8·40	8·80
CaO, Cu, Se, As, loss	1·18	0·15	1·23	1·36	0·73
Specific gravity	2·76	3·15	2·67	2·56	2·85

The value of the slates does not depend upon their appearance,

not easily oxidized, but upon that of iron sulphide in an ext
fine state of division, which exists especially in the last two
ties. These decompose so completely that after a few years n
but loose carboniferous silica is left behind. From this it f
that the calcining of the copperas-slates (formerly employe
only did no good, but much harm, by driving off a good
sulphur as SO_2. The largest plant for producing the cop
slate is at Hromic, where a seam of 20 fathoms thickness ex
a depth of 11 fathoms. Between the years 1831 and 1871 65
tons of suitable ore were got here; and altogether about 9
lions of tons are available. At Littau there are about 7 m
of tons; and so forth. The ore is broken up pretty equa
stone-breaking machines, and tipped into large terrace-s
heaps, leaving both horizontal and perpendicular air-cha
By means of a system of spouts water can be sprinkled al
The process of oxidation by weathering lasts about three
and very large heaps having been made at first, strong ly
always obtained. The ores, on lying in the moist air, grov
the pyrites is oxidized, first to ferrous sulphate, then to ferr
phate, along with a little aluminium sulphate. These salts, tog
with the pre-existing soluble salts, are lixiviated by water con
in the above-mentioned spouts. The brown liquors, posses
density of generally 28°, and up to 38° Tw., are run into w
reservoirs, where they remain some time for settling and are a
concentrated by spontaneous evaporation and also more highl
dized. Then they are concentrated, by top-heat in brick fur
up to 77° Tw.; the soot and ashes are allowed to deposit in set
tanks; and the clear liquor is further evaporated in cast-iron b
to a sirupy consistence. If then run onto the floor, it solidi
crude vitriol stone. This is a hard, pale green or yellowish-
mass, containing still a good deal of ferrous sulphate and wa
crystallization. In order to remove the latter and to oxidi
former, it is calcined in open roasters. The *calcined vitriol*
is essentially anhydrous ferric sulphate; it is yellowish white
solves in water with a reddish-yellow colour without leavin
large residue; and the solution has a strongly acid reaction
still contains a little ferrous sulphate and constantly, in va
quantities, aluminium sulphate along with a little magnesiur
calcium sulphates. The production of vitriol stone at Hr

Littau, and Weissgrün in 1872 amounted to about 3000 tons; it takes from 6 to 20 tons of slates to make one ton of vitriol stone. The stone formerly only yielded about 33 per cent. of "oleum;" now, however, owing to improved processes, it yields from 40 to 50 per cent.

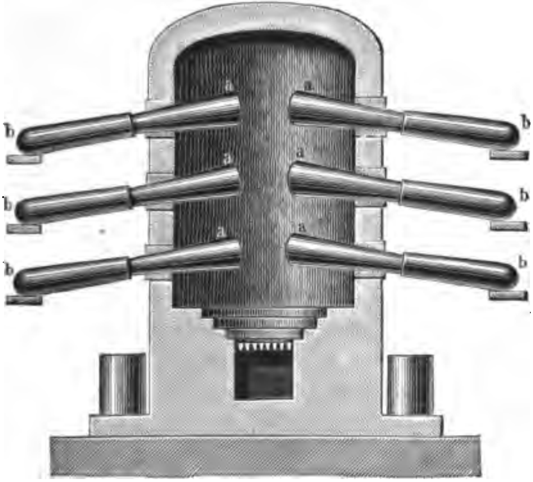
The firm of J. D. Starck works up the stone in 4 works, altogether with 120 "oleum-furnaces." These are the galley furnaces, well known from older technological works. The calcined vitriol stone is broken by crushing-rollers and charged into the oleum-retorts, made of fireclay. On each side of the galley furnace there are four tiers of 34 retorts each, the bottoms of those in the centre nearly touching one another. A fifth tier is formed at the top by 34 large retorts, open at either side, reaching right across the furnace, and at each side provided with a receiver. Each of the smaller retorts also is connected with a receiver, large enough for holding the product of 4 or 5 distillations. The necks of the receivers are narrower than those of the retorts; they are put into the latter, and the joint plastered with clay. Such a furnace thus contains 272 small and 34 large oleum-retorts and 340 receivers. The lower part of the furnace, where the fireplace, grate, and ash-pit are located, is made of solid masonry; the upper part consists of a light arch, perforated for each retort in such a way that the necks of these hold them without any further support. The bottom tier of the receivers rests upon the brickwork, the higher tiers on wooden laths.

Into each retort is ladled, on the average, 750 grms. of vitriol stone. The yearly consumption at Starck's works is 724,000 retorts and 40,000 receivers (formerly twice as much). They are made at private potteries near the works, and thus only cost about 1*d.* to 1½*d.* a piece, whilst formerly, when bought abroad, they cost about 3*d.* each.

At the beginning of the distillation the temperature is slowly raised, so that after 4 hours the bottom tier of retorts has only attained a red heat. During this time the retorts are left open; and consequently nearly all the ferrous sulphate still present is oxidized to ferric sulphate. With a higher heat there appear at the mouth of the retorts aqueous vapour and sulphurous acid, generated from aluminium sulphate and still existing ferrous sulphate. Now thick vapours of sulphuric anhydride follow, which gives the sign for putting on the receivers. As the ferric sulphate mixture of SO_3 and SO_4H_2, or rather of pyrosulphuric acid ($H_2S_2O_7$) with sulphuric acid, some liquid containing water must be put into the receivers, in order to condense and dissolve the sulphuric anhydride. This may be either rain-water, or ordinary (so-called "English") oil of vitriol. In the former case each receiver gets ½ lb. of water, and it takes 4 or 5 distillations from the retort to attain the usual concentration of the oleum (79° Baumé). When the receivers have been charged with "English" oil of vitriol, of 66° Baumé (=170° Tw.), it only takes 3 or 4 distillations to get it up to 80° Baumé.

When the oleum has reached sufficient concentration, which the workmen recognize from the speed with which a wood splinter, dipped into it, is charred, it is filled into stoneware bottles and left for a week to settle, after which time the clear acid is drawn off from the deposited mechanical impurities. The specific gravity is sometimes artificially increased by addition of anhydrous sodium sulphate, to which practice, as Mr. E. V. Jahn in his report naïvely remarks, the consumers decidedly object. When "English" oil of vitriol has been put into the receivers, the oleum of course contains the well-known usual impurities of the former.

The ferric oxide remaining in the retorts (about 33½ per cent.) is known by the name of caput mortuum, colcothar, English red, &c. (In England a similar article is called "Venetian red.") It is raked out of the retorts after each distillation, and exhibits different colours according to the degree of heat to which it has been exposed. The lower tiers supply it of darker, the upper ones of lighter colour. In the crude state it was very difficult to sell as a common pigment or polishing-powder; in 1832 about 250 tons of it were sold. J. D. Starck has very much improved this article by proper treatment; so that in 1872 1000 tons of it were sold, of 19 shades and 41 kinds; it is especially used at Hamburg for painting ships. At the Bras works it is ground under French mill-stones and again calcined with the addition of common salt and at a certain temperature. The yellow shades are obtained by an addition of 2 per cent. of salt, igniting for an hour, and gradual cooling in a closed space; the brown ones, by adding 4 per cent. of salt; the purple ones, by 6 per cent. of salt, igniting for 6 hours at a gradually increasing heat, and rapid cooling. The igniting takes place in fire-clay pipes lying in galley furnaces similar to the oleum-furnaces, each of them con-



the receivers getting cold. The fire is then allowed to go out, the furnace allowed to cool for 12 hours, the hardened luting broken by a few taps with an iron tool, and the receivers taken off. The contents of the latter are not emptied into the well-known stoneware bottles, closed by screw-plugs, until they have become sufficiently concentrated—that is, after 4 or 5 operations (see above); the retorts, however, are cleared out every time, by raking out the caput mortuum, and are tested by tapping to see whether they are still sound. If not, they are replaced and the distillation at once begun with a fresh charge. Formerly each distillation in a furnace of 288 retorts required 30 new retorts and 3 new receivers; now there is less breakage. The fuel is wood well dried, or lignite.

Payen gives the following cost-account for 100 kilog. oleum (now probably obsolete) :—

	frs.	ct.
250 kil. vitriol stone	14	0
2000 kil. lignite	3	0
Wages	8	0
4 retorts and 4 receivers (?)	2	0
Interest................................	1	80
	28	80
125 kil. residue, value..............	2	0
Cost of 100 kil. oleum..............	26	80

Sometimes the acid from Bohemian vitriol stone is black and must be decolorized by the addition of a little nitric acid, which diminishes its value, since the nitric acid cannot be totally removed again.

The acid which is used in the manufacture of artificial alizarine must be still richer in anhydride than the best oleum as it came from Bohemia up to the last few years. This so-called "*solid sulphuric acid*" the alazarine-manufacturers formerly made for themselves by heating the oleum in cast-iron retorts and receiving the escaping anhydride in another part of the acid, contained in iron vessels entirely protected from the access of air; but now Starck's works regularly supply a solid acid with 40 to 45 per cent. SO_3, which is almost pure pyrosulphuric acid; and they are now said to sell also *pure anhydride* in soldered-up tin cans (similar to the London or G. C. Zimmer's article, see below).

Fuming sulphuric acid from sodium bisulphate.—Prelier (Engl. Patent, June 29th, 1847) has proposed to prepare fuming oil of vitriol by the following process, which is said to have been carried out in France on a large scale (hardly permanently). 100 parts of calcined sodium sulphate are mixed with 2 parts of potassium sulphate and 2 parts of gypsum, charged into retorts of sandstone (?), and a sufficient quantity of concentrated sulphuric acid added to form bisulphates. Then heat is applied; first all the water distils over, then sulphuric acid of 77°, then of 106°, then of 170° Tw., and at last fuming acid. The latter is known by the drops falling into water producing a hissing noise; then a receiver filled with acid of 170° Tw. is put on. This acid sometimes contains sodium sulphate. The residue in the retort is always used for the same purpose. The acid made in this way is said to cost only half as much as that made from copperas (?). Exactly contrary to this is the assertion of a young engineer, Schemfil, who on Dec. 2nd, 1869, took out a French patent for the continuous manufacture of fuming oil of vitriol from calcined copperas in closed vessels (Moniteur scientif. 1870, p. 492; it is evidently a tiro's proposal); he calculates that the acid made by the process usual in France from sodium bisulphate costs 100 to 140 francs for 100 kilog., but the acid made at Nordhausen (where for a long time none has been made!) only 8 to 12 francs for 100 kilog. His statements are in every respect improbable.

Wallace obtained an English patent (May 30, 1876) for heating sodium bisulphate in fire-clay retorts; the formed anhydride or fuming vitriol is to be collected in earthenware jars with a lid perforated for receiving the gas-pipe, which can be replaced by a plain cover; thus the acid can be sent out in the receiver itself, and the fumes emitted in pouring it from one vessel into another are avoided. The fumes first coming over, which consist of aqueous sulphuric acid, are condensed separately. The sodium sulphate remains in the retort, and is always reconverted into bisulphate by adding sulphuric acid; so that continuous operation is possible.

It is very probable that the manufacture of pyrosulphuric acid and anhydride, latterly carried out in Germany and England, but thus far kept very secret, is founded upon the application of bisulphate, probably combined with Winkler's method (see below) for recombining the SO_2 and O formed in the operation; possibly other metallic sulphates are employed for the same purpose. It is said that partly platinum apparatus, partly other material is employed —the former no doubt with special precautions; for, under ordinary circumstances, on decomposing bisulphates in platinum-lined earthenware vessels 1 gram of platinum is dissolved for each kilogram of pyrosulphuric acid (Scheurer-Kestner, 'Comptes Rendus,' 29th April, 1878), which would make the acid much dearer than is indicated by its present price (£65 per ton of pure SO_3).

Fuming sulphuric acid from the action of boric acid upon sodium bisulphate (Kerl-Stohmann, 'Chemie,' 3rd ed. vi. p. 156).—This method has probably never emerged beyond the state of a suggestion.

From magnesium sulphate, either the natural anhydrous salt, or that made by calcining Epsom salts (Sonstadt's patent, March 3rd, 1875). The operation was to be carried out in the same way as with ferric sulphate. Wagner (Jahresb. 1876, p. 327) observes that the experiments formerly made by igniting calcined kieserite produced very little sulphuric anhydride, but very much sulphurous acid and oxygen.

From magnesium sulphate and sodium pyrosulphate mixed.—Wolters has obtained a German patent (No. 3110, March 5th, 1878) for this process. $MgSO_4$ acts upon $Na_2S_2O_7$ considerably below a red heat, a double salt ($MgSO_4$, Na_2SO_4) being formed, and SO_3 being liberated. Instead of Na_2SO_4, K_2SO_4 &c. may be employed. The remaining salt is reconverted into the mixture first employed by treatment with water and ordinary sulphuric acid, and exposing to sufficient heat. The value of this process is said to consist in the fact that the anhydride is liberated at a much lower temperature than from sodium pyrosulphate alone, thus preventing much loss, causing a larger yield of SO_3, and permitting the use of ordinary fire-proof materials without any extraordinary wear and tear. (Experiments made in the author's laboratory with Wolters's process have to a great extent confirmed these statements.

The preparation of sulphuric anhydride and of fuming acid by catalytic action.

By this, now-a-days not very scientific-looking expression we will designate all those syntheses of SO_3 in which the action of the mediating substance cannot be traced, but the union of SO_2 with O *seems* to result from mere contact with another substance. Formerly it would only have been necessary to mention the many proposals of this kind in a few words, just as we shall do later on with the other, hitherto sterile, proposals for making sulphuric acid otherwise than by the usual chamber-process. But as Cl. A. Winkler in 1875, by his original treatment of the matter, gave it a practical shape, the labours of his predecessors must be also mentioned rather more explicitly.

Phillips (who already on March 31st, 1831, had taken out an English patent for uniting SO_2 and O by ignited platinum &c.) and *Magnus* (Poggendorff's 'Annalen,' xxiv. p. 610) observed in 1832 that a mixture of 2 vols. of sulphurous acid and 1 vol. of oxygen gas, which in the dry state remains unchanged, is gradually condensed in the presence of water, but much more quickly in the presence of ignited platinum. If the moist mixture of SO_2 and O or atmospheric air is conducted through a darkly red-hot tube containing platinum sponge or wire, nearly all the SO_2 is condensed to oil of vitriol; dry platinum black converts the mixture into fuming acid (Doebereiner, ib. p. 609). Magnus even observed the formation of a little sulphuric acid on conducting the mixture through a darkly red-hot tube containing broken glass—and, in a smaller degree, through an empty tube; Mahla certainly could not confirm this. Blondeau (Compt. Rend. xxix. p. 405) found in 1849 that darkly red-hot argillaceous sand has the same effect upon a moist mixture of SO_2 and O.

The formation of *anhydride* under these circumstances had been already noticed by Phillips and Magnus; and Doebereiner's above-found in 1852 (Ann. Chem. Pharm. lxxxi. p. 255) that the oxides of copper, iron, chromium, best of all a mixture of chromium and cupric oxide, brought to a low red heat, caused the formation of thick fumes.

Platinum as sponge and sheet did not act at ordinary temperatures; but it acted far below red heat, copper sponge only after superficial oxidation. Woehler's results gave an impetus to several trials on the large scale (for instance, at the Oker works), which, however, remained fruitless (Wagner's Jahresb. for 1859, p. 144), because the time required for the reaction was too considerable. No more success was attained by Schneider's process, with platinized pumice, much praised in 1848 (Dingler's Journ. cvii. pp. 159, 363, cix. p. 354), and the trials of Plattner (Die metallurgischen Röstprocesse, p. 339) and Reich (Dingler's Journ. ccxvii. p. 230), both the latter made at the Mulden works with ignited quartz as the catalytic substance. Exactly the same process has been again proposed by Piria ('Cimento,' ii. p. 293; Liebig's 'Jahresb.' 1859, p. 308), evidently only for laboratory use, as the sulphurous acid was to be made from sodium sulphite and dilute sulphuric acid; and not atmospheric air, but oxygen was to be employed. Kuhlmann once more patented the same method in 1858; other patents, by Laming (1848), Robb (1853), Trueman (1854), Schmersahl and Bouck (1855), alike contain nothing new.

Most of these proposals were made with the object of replacing the lead-chamber process by one believed to be simpler and better, and did not aim at the production of sulphuric anhydride or fuming oil of vitriol, but of ordinary sulphuric acid. Thus, for instance, Phillips (see above) proposed to drive sulphurous acid, made by the combustion of sulphur, and mixed with an excess of atmospheric air, by means of a blowing engine through a nearly red-hot cast-iron tube filled with platinum sponge or finely rolled-up platinum wire; the sulphuric acid vapour, formed therein, was introduced, along with the nitrogen and the atmospheric air present in excess, at the bottom of a long upright lead cylinder filled with pebbles, over which water continually trickled down for condensing the sulphuric acid. In order to save the expensive use of platinum alone, Piria proposed pumice impregnated with platinum salt and ignited; and most of the other inventors enumerated above propose to do altogether without platinum. But all these attempts failed;

the reaction was too slow and imperfect, and altogether incapable of competing with the ordinary lead-chamber process.

The matter takes a different aspect, when the question is not that of competing with the lead-chamber process for ordinary vitriol, but with the vitriol-stone process for fuming acid, or even to make sulphuric anhydride itself on a manufacturing scale. This latter had never been done till the most recent time; and the fuming acid is made in Bohemia exactly in the same way as it was nearly a century ago, with an enormous expenditure of labour, fuel, space, and vessels, and on a very small scale, only enlarged by repetition of the apparatus. Although these circumstances and the fact of being dependent upon the occurrenee of copperas-slates had gradually given a monopoly of the manufacture of fuming vitriol into the hands of that single Bohemian firm, its use has recently very much increased, since fuming acid has been employed for purifying ozokerite, for the manufacture of benzenedisulphonic acid, anthracenedisulphonic acid, and other organic sulpho-acids serving as intermediate stages in the manufacture of sundry colouring-matters. It could be predicted with certainty that this powerful chemical agent would acquire eminent technical importance as soon as the monopoly of its production was broken. It is the great merit of Professor Cl. A. Winkler to have brought this question to a focus in 1875 by a fundamental research (Dingler's Journal, ccxviii. p. 128; Wagner's Jahresb. 1875, p. 296), the contents of which I give in abstract, as follows:—

Winkler, in the first place, proposes to emancipate the manufacture of oleum from local circumstances, such as the occurrence of copperas-slates, by making vitriol stone by the treatment of ground caput mortuum with concentrated oil of vitriol. These two bodies unite on gentle heating to a yellowish-white hard mass of ferric sulphate. The water of the sulphuric acid is evaporated by the heat developed in the reaction itself, without any external heat being applied, if quantities not too small are employed and the proper proportion of 1 part of caput mortuum to 1·8 part of acid is observed. If, instead of acid of 170° Tw., chamber-acid be used, the mixture of this with ferric oxide still hardens on prolonged heating to vitriol stone, the water being volatilized. The caput mortuum can be replaced by any other form of ferric oxide, such as burnt pyrites, if pure and very finely ground. The ferric oxide is always recovered again on distilling the oil of vitriol, and can be used over again for producing fresh vitriol stone.

The distillation of oleum, however, is a process little suited for working on a large scale. The bulky apparatus and the difficulty of managing it justly deter any one from trying to apply it elsewhere than where it has been practised of old. The manufacture of oleum can only become general by sulphuric anhydride being no longer produced by heating certain anhydrous sulphates, but directly from sulphurous acid and oxygen by catalytic action. The possibility of this had been proved long ago; and the principal difficulty was that of choosing the fittest substance for the contact action. This must in any case be platinum in a fine state of division; but, on account of its costliness, it must be spread over an indifferent surface, by which, also, its activity will be increased. Most highly to be recommended for this purpose is platinized asbestos, obtained by soaking soft, loosely felted asbestos with a concentrated solution of platinum chloride, then dipping it in a solution of sal ammoniac, drying and igniting it. Much less efficient are other contact substances impregnated with platinum, such as pumice or porous earthenware.

The action of heated platinized asbestos upon a mixture of SO_2 and O may under certain circumstances lead to a very strong formation of anhydride; but it is not so in the presence of other diluting gases, as the following experiments show. The platinized asbestos was of a soft, woolly texture, and contained 8·5 per cent. of platinum. It was employed in a tube heated to a low red heat, in a layer 12 inches long and ½ inch thick. The dried gaseous mixture entered at one end of the glass tube, passed over the asbestos in a moderately quick current, and at the other end was first conducted into water, then into a solution of sodium carbonate. Of 100 parts SO_2 employed, there were converted into SO_3 on the application of,

1st, a mixture of pure SO_2 and pure O	73·3 parts.
2nd, „ „ SO_2 and air	47·7 „
3rd, a gas with 4 per cent. SO_2 by volume, obtained by burning sulphur in a current of air	11·5 „

Thus the action of the platinized asbestos, and probably also that of all other contact substances, is lessened to the same extent as the dilution of the sulphurous acid by indifferent gas increases; and an excess of sulphurous acid or oxygen beyond the stoichiometrical proportion of SO_2 and O must also be regarded as such.

Now it is well known that the *ordinary strong sulphuric acid decomposes at a strong red heat into sulphurous acid, oxygen, and water.* Of these the water can be easily and completely condensed, and there remains a mixture of SO_2 and O exactly in the proportion necessary for forming SO_3. In this way every admixture of indifferent gas could be avoided; and the SO_2 and O could be reunited by catalytic action, and thus the sulphuric hydrate be indirectly converted into anhydride. In order to carry this out experimentally, the following apparatus was constructed. A wrought-iron tube was covered inside and outside with a mixture of fireclay and waterglass; this was burnt in, the tube filled with bits of porcelain, and then brought to a strong red heat in a charcoal furnace. Into a cork at one end a bent funnel-tube was inserted, through which sulphuric acid of 170° Tw. was continuously dropped in; its supply was regulated by a Mariotte's bottle and a screw clamp. The sulphuric-acid vapour generated, passing through the red-hot tube filled with bits of porcelain, was decomposed, although not completely, into SO_2, O, and H_2O. The latter was retained in a vessel filled with pumice soaked with strong sulphuric acid, together with the undecomposed sulphuric acid. The remaining dry mixture of SO_2 and O entered a long glass tube bent downwards at the further end, the horizontal part of which was filled with platinized asbestos, whilst the vertical branch entered a receiver filled with strong sulphuric acid. This was succeeded by a second similar receiver, and this by a receiver filled with a solution of sodium carbonate for the absorption of SO_2. As soon as the platinized asbestos had, by means of a gas-furnace, been brought to a low red heat, an ample formation of sulphuric anhydride was observed, which partly condensed in a solid state in the tubes. The operation went on regularly, without any special supervision. After several hours the experiment was interrupted, and the contents of the first receiver were found entirely converted into fuming vitriol. It was ascertained that 93 per cent. of the sulphuric acid employed had been decomposed, and of the quantity decomposed 78 per cent. had been combined into SO_3.

For carrying out this process on a large scale Winkler proposes the following apparatus:—The decomposition of the sulphuric acid is to take place in a furnace containing fireclay retorts, similar to filled with large bits of quartz, fire-bricks, potsherds, &c., and carry the usual mouthpiece with a pipe for taking away the gas. At the other end a wrought-iron Welter's funnel tube is to be fixed. Through this, while the furnace is in full red heat, a continuous jet of strong sulphuric acid is run in (possibly a weaker acid might do), and in the red-hot retort is immediately vaporized and decomposed. Perhaps upright retorts would answer the purpose still better. [Very probably it would be preferable to evaporate the sulphuric acid in separate vessels.] The mixture of SO_2, O, and aqueous vapour thus obtained in a constant stream is conveyed from the different retorts into a main tube serving as receiver, and passes from this into the condenser, in which the greater part of the water as well as the sulphuric acid carried away is condensed. The condenser would suitably consist of a system of lead pipes, cooled by air or water, similar to the condensers at gas-works. The sulphuric acid running away from it, and perhaps showing 22° to 33° Tw., which must be strongly charged with sulphurous acid, would be returned to the chamber-process. The gaseous mixture is then dried in one or, if necessary, in two coke-towers, by a spray of sulphuric acid of 144° Tw. It can now be exposed to the action of the ignited asbestos, of which 50 to 100 kilog., containing 4 to 8 kilog. platinum, would suffice for a pretty large manufacture. A diminution of the contact-action, which it has been feared might take place in time, could only be caused by ashes, dust, soot, &c., none of which can come into action here; besides, the platinum, if necessary, could easily and cheaply be extracted and transferred to fresh asbestos. The action of the platinized asbestos on the mixture of SO_2 and O begins at a scarcely visible red heat; and therefore, on the large scale, the heat of the fire-gas escaping from the furnace for decomposing the sulphuric acid will be available for this purpose. This fire-gas is conducted through a muffle-shaped space built upon the first furnace, in which several fireclay pipes, glazed with a porcelain enamel, are placed, loosely filled with platinized asbestos. The gas enters this after leaving the drying-tower; the sulphuric anhydride formed is conveyed away by similarly glazed stoneware pipes, and either condensed as such or dissolved in ordinary strong vitriol, to make this fuming. If the latter has to be done, the vapours of the anhydride are allowed to enter a tower fitted with ridges of lead jagged out at the bottom, over which a latter is so regulated that the acid leaves the tower in the fuming state, and can be at once filled into carboys. Possibly this last operation requires the combined action of several towers, in which case they are best placed one on the top of another, so that the acid can run from one to the other and become gradually saturated. Even if on the large scale the union of SO_2 and O should not take place completely, the remainder of the gaseous mixture can be introduced into the lead chamber, and here condensed in the usual manner by itself.

Winkler adds the remark that the mixture of SO_2 and O may be just as well generated by strongly heating vitriol stone or other anhydrous sulphates in large vessels, such as the retorts employed in zinc-making, and transformed, by means of platinized asbestos, into sulphuric anhydride. Then, to be sure, a residue would have to be dealt with; but, on the other hand, the drying of the gas would be saved, and at all events the drawbacks of the present manufacture of oleum would be avoided. [A proposal quite similar to this (certainly the least essential) part of Winkler's process, was made by Prelier in 1847 (see p. 638).]

Squire and Messel have taken out an English patent for a process exactly like that of Winkler, except that they prescribe the use of platinized pumice in the place of asbestos. Their patent dates from Sept. 18th, 1875, and was, of course, only published six months afterwards, whilst Winkler's publication, written some time before and based upon experiments made in the course of more than twelve months previously and known to all his Freiberg students, appeared in the October number of 'Dingler's Journal' of the same year.

In a later publication (Dingl. Journ. ccxxiii. p. 409) Winkler mentions that Debray ('Les Mondes,' 1876, No. 3) had objected to his process that it was not suited to the manufacture of oleum on the large scale, on account of the great difficulty of decomposing the sulphuric acid at a high temperature, and of the rapid destruction of the vessels. Neither metal nor earthenware vessels resisted the sulphuric-acid vapours at such temperatures; and even platinum was permeable to gases at such a heat, and would be much damaged by the action of the flame and the impurities of the sulphuric acid. To these objections Winkler replies that he had decomposed his sulphuric acid in iron tubes without any difficulty, and that even to run into the red-hot retort itself, but onto a porous layer of alumina or ferric oxide, in which it is absorbed in order to be at once vaporized again. Debray himself mentions that in the laboratory of the École Normale at Paris 3 kilog. of sulphuric acid per hour were decomposed in a platinum tube of 120 centims. length and 25 centims. diameter, without mentioning whether this was filled with bits of porcelain or bricks. In a decomposing-vessel of the size of a gas-retort at least five times as much, say 15 kilogs. per hour, could be decomposed—therefore, in a furnace with five retorts, 75 kilogs. per hour, or 1800 kilogs. (=36 cwt.) daily, which, at the rate of 75 per cent. of anhydride, would amount to a yield of 1000 kilogs. of the latter, or, by dissolving it in strong vitriol, of 2500 kilogs. (=2½ tons) oleum. Four such furnaces would be able to cover the whole present make of 3000 tons oleum per annum. Winkler also considers it remarkable that Debray should make the above objections; since he and Deville in 1861 had recommended the decomposition of sulphuric acid as the cheapest source of oxygen, and several others had followed them; their process, as is well known, was exhibited in a special laboratory at the Paris Exhibition of 1867, but certainly was discontinued directly after. Winkler complains that, if Debray had found his own rather too confidently made statements to be erroneous, he should have corrected them himself. [Such things do happen elsewhere as well!]

As far as can be learned from practice, it is just the two difficulties mentioned by Debray which militate against the process, especially the decomposition of the sulphuric acid. Still several factories in Germany and one in England already work according to a process different from that of Winkler in but few essential points; and even pure anhydride, of 98 per cent. SO_3, is sent into the trade by several firms. This beautifully crystallized product is packed in tin cans of a little more than 1 cwt., and sold at present at 2*s*. 6*d*. per kilog. of pure SO_3. It is prepared by redistilling manufactured pyrosulphuric acid. More frequently a mass containing 40 per cent. anhydride (that is, nearly pure pyrosulphuric acid) is sent out in drums of 2 cwt.; it was sold in April 1878 at £95 per ton; in April 1879 it only fetched £65 per ton,—both calculated as pure SO_3.

J. Neale (English patent of March 14th, 1876) heats anhydrous sulphates or bisulphates of iron, zinc, aluminium, or sodium in earthenware retorts or muffles, and conducts the mixture of sulphurous acid and oxygen formed by their decomposition over heated spongy platinum, or the oxides of chromium, iron, or copper, or any other substance which may cause the mixture to combine into sulphuric anhydride. The latter is then condensed by itself or utilized for fuming oil of vitriol by receiving it into ordinary strong sulphuric acid. It is quite possible that this process is employed by some of the manufacturers who bring this article into the market now.

According to a recent patent by Dr. Messel (Jan. 15th, 1878), brimstone is to be burnt in a current of oxygen, obtained by the electrolysis of water by means of a dynamo-electric machine. The SO_2 formed, with the excess of oxygen required for forming SO_3, is passed into a gas-holder; and from this the gases are passed at an elevated temperature over platinum sponge, platinized asbestos, chromic, ferric, or cupric oxide, &c. The SO_3 formed is collected by itself or absorbed in SO_4H_2. By employing two gas-holders the process becomes a continuous one. The electrolytic hydrogen generated at the same time is employed for heating, or, after being carburetted, for lighting. [This process seems to be far too expensive to be of any practical value.]

The greatest difficulty in Winkler's process for manufacturing fuming oil of vitriol or anhydride, and in all other processes started in consequence of the impetus given by him, is the material of the vessels to be employed. Wallace, in his above-mentioned patent, proposes to employ glazed plumbago retorts. Most, if not all, actually working factories seem to employ platinum vessels, which certainly are strongly acted upon, as is shown by Scheurer-Kestner (see above). The extent of this action will partly depend upon the amount of arsenic and nitrous compounds contained in the sulphuric acid (comp. Wagner's 'Jahresbericht,' 1877, p. 238), partly also upon the special construction of the apparatus.

(So far the apparatus actually employed in the manufacture of fuming oil of vitriol or anhydride by the contact process has been kept strictly secret by the manufacturers; but the author will be able to describe it in some detail in the appendix at the end of Vol. II., where also a new method, by Professor Winkler, will be described, of which he has at present only private knowledge, and by which sulphuric anhydride can be made on an industrial scale from burner-gases containing as little as 4 per cent. SO_2.—April 1879.)

CHAPTER XVIII.

OTHER PROCESSES FOR MANUFACTURING SULPHURIC ACID.

All the other processes which have been proposed for producing sulphuric acid, numerous as they are, can be dismissed with a very few words, since none of them has had the slightest technical success or promises to become successful in future. The details can be found in the places quoted.

I. *Oxidation of Sulphurous Acid by means of Nitrous Acid, but without Lead Chambers.*

(*a*) Proposals for replacing the lead chambers by chambers made of india-rubber, gutta percha, slate, "zeiodelite," glass, &c. have been mentioned on p. 262.

(*b*) MacDougal and Rawson (patent of Nov. 21st, 1848) conduct sulphurous acid and air through nitric acid contained in a Woulfe's bottle, in which sulphuric acid and hyponitric acid are generated; the latter, with the air in excess, passes through several vessels filled with water, in which the nitric acid is regenerated.

(*c*) Hunt (patent of Aug. 16th, 1853) conveys a mixture of sulphurous acid and air through a tower filled with pebbles, in which nitrous vitriol continuously trickles down. This principle had already been proposed by Gay-Lussac; and it is actually carried out in the Glover towers, so far as it is practicable—that is, by conducting the escaping gases into lead chambers.

(*d*) Persoz ('Technologiste,' xvii. p. 461; 'Dingler's Journal,' cxxxix. p. 427; Wagner's 'Jahresbericht,' 1856, p. 54) passes sulphurous acid through nitric acid diluted with from 4 to 6 volumes of water, and heated to 100° C., or through a mixture of nitric acid or a nitrate with muriatic acid, in a comparatively small glass or stoneware vessel, promoting contact by an agitator. The gases generated by the reduction of the nitric acid ascend in condensing-towers, where they are regenerated into nitric acid by an ascending current of air and a descending jet of water. The sulphurous acid might even be diluted with carbonic acid, nitrogen, or other gases. In theory this process is right enough; in practice it is said to have failed principally from the difficulty of constructing vessels suitable for resisting the acids (?).

(*e*) Verstraet's tubular apparatus ('Bulletin de la Société d'Encouragement,' 1865, p. 531; 'Dingler's Journal,' clxxix. p. 63; Wagner's 'Jahresbericht,' 1865, p. 226) has been mentioned previously. The Jury Report of 1851 asserted that similar stoneware vessels, constructed by Fouché-Lepelletier, were at work at Javel, near Paris, and that in that factory one third of the annual make of 3600 tons was produced in them, with one third of the cubic contents and at one eighth of the cost of lead chambers. This assertion has been proved to be entirely erroneous by original correspondence in Hofmann's 'Report by the Juries,' 1862, p. 8.

(*f*) Lardani's apparatus (Bull. Soc. Chim. viii. p. 295; Chem. News, 1868, No. 441, p. 238) has also been described above; it exemplifies no essentially novel principle.

(*g*) Kuhlmann (English patent, Dec. 11, 1850) proposed to force a mixture of sulphuretted hydrogen (from soda-waste) and air through nitric acid, by which nearly all the sulphur was said to be oxidized to sulphuric acid.

(*h*) Petrie (English patent, Aug. 11, 1860) employs a system of stoneware pipes filled with pebbles, through which a current of nitric acid passes from one side, and one of SO_2 and air from the other, the quantities of the materials and the construction of the apparatus being arranged in such a manner as to avoid any loss of nitric acid.

II. *Processes dispensing with nitre.*

(*i*) Gossage (Patent of Oct. 6th, 1857) burns sulphuretted hydrogen from soda-waste, cools the products of combustion, allows them to ascend in a coke-tower fed with water, runs the solution of sulphurous acid thus obtained down another coke-tower supplied with

the remaining SO_2 into a lead chamber, where it
oxidized in the usual way. According to Gossage'
(Hofmann, Report, p. 9) this process is not practical

(*k*) Petrie (Patent of Nov. 1st, 1852) allows a m
phurous acid and water, heated to 300°, to meet a s
in pipes of earthenware or iron filled with silica, or
platinum, &c.

(*l*) The observations of Doebereiner, Phillips
Blondeau, &c. on the formation of sulphuric acid
action" have been mentioned already on p. 640—an
Woehler and Mahla (Ann. Chem. Pharm. lxxxi. p.
ing to which a mixture of SO_2 and O is converted i
acid (anhydride) not only by platinum, but also by
copper, iron, or chromium at a low red heat. The
hope that this reaction would become practical. A
of attempts have been made in this direction, some
been mentioned in the last Chapter. To this categ
mentioned proposals of Gossage and Petrie are i
referred, and those of Schmersahl and Bouck (pat
1855) and of Schneider (see preceding Chapter). All
of this kind have remained equally sterile with the c
cesses enumerated in the present Chapter, so far as
supplanting the lead-chamber process by a new on
not be confounded with Winkler's successful utiliza
lytic action" for making anhydride, as he alway
sulphuric acid made in the ordinary way by
process.

(*m*) Hähner (Patent of March 28, 1854) emplo
the presence of aqueous vapour for oxidizing SO_2.
cess has been patented by Macfarlane (Jan. 14, 186

III. *Sulphuric Acid from Sulphates.*

As already mentioned on p. 39, the neutral sul
alkalies, the alkaline earths, and lead are as good as
at a red heat. The acid (primary) sulphates of th
first changed into pyrosulphates ($2NaHSO_4 = Na_2S_2O$

the latter afterwards split up into neutral sulphates and sulphuric anhydride. This reaction, for obvious reasons, cannot be employed for the manufacture of sulphuric acid proper, but only for that of fuming acid, under which head it has been spoken of.

Most of the other sulphates are no better adapted for the manufacture of sulphuric acid. Only those whose metallic radicals are but very slightly positive, more particularly those which, according to the assumptions of modern chemistry, represent a sexivalent group formed by an internal linking together of two quadrivalent atoms (that is, especially ferric oxide and, though less so, alumina), and the *acid* sulphates of other radicals, yield up their sulphuric acid at a comparatively low temperature, and consequently all or the greater part of it undecomposed; the other sulphates split up at a much higher temperature, mostly decomposing into metallic oxides, sulphurous acid, and oxygen, yielding only a small portion of their sulphuric acid as such or as anhydride. Even if it were otherwise, their high price would make their employment for the manufacture of sulphuric acid impossible; most of them are themselves produced by means of ready-made sulphuric acid. From even the cheapest and most easily decomposable of all the sulphates in question, ferric sulphate, only fuming oil of vitriol can be made, and that only under especially favourable circumstances, as shown above.

There only remain the sulphates occurring in some abundance in nature as such, viz. those of baryta and lime. The former of these has hardly ever been seriously taken up for this purpose; but the sulphate of lime (gypsum) has very frequently been so.

Sulphuric Acid from Gypsum.

The enormous quantities of sulphuric acid occurring in nature in the shape of gypsum, and nearly worthless in this form, have occasioned many proposals for their technical utilization. These, however, have never met with any success; and least of all can any prospect of it be held out now-a-days, since such abundance of cupreous pyrites has been discovered, with which, so far as can be seen, no other material can compete in cheapness.

(1) *Production of sulphurous acid from gypsum.*—Tilghman (English patent, Feb. 1st, 1847) passes steam over red-hot gyp-

to escape.

Cary-Mantrand (Barreswil and Girard, Dictionn. de Chim. industr. i. p. 37) exposes ignited gypsum to a current of dry HCl (whence does he get this?). $CaCl_2$ is formed; and SO_2, O, and SO_3 escape.

O. Siemens (Dingl. Journ. clxix. p. 207; Wagner's Jahresb. 1863, p. 208) decomposes a fused mixture of gypsum and common salt by steam. There remains behind basic calcium sulphide with a little Na_2S, Na_2SO_3, and $Na_2S_2O_3$; the gases given off are SO_2, HCl, and H_2S; the latter is removed by conducting CO_2 and steam at the same time into the melted mass (?). This process is the subject of strongly adverse criticism by Buff (Wagner's Jahresb. 1864, p. 170), who shows that the decomposition observed has been produced merely by the red-hot iron which forms the material of the apparatus.

Kuenzi (Wagner's Jahresb. 1858, p. 95) fluxes gypsum with quartz, sand, clay, &c. to an easily fusible slag, whilst SO_2 and O escape.

O. Schott (Dingl. Journ. ccxxi. p. 442) ignites sodium sulphate, gypsum, and coal, in order to obtain a frit for glass-making; the SO_2 is to be conveyed into a lead chamber along with the other gas and converted into sulphuric acid.

Martin (Bull. Soc. Chim. xxi. p. 47) prescribes making an artificial sulphide by smelting 1700 parts of gypsum, 1000 of ferric oxide, and 500 of coal in a blast-furnace; this is to be burnt like natural sulphides. In this case *at most* a monosulphide of iron will be obtained; and that will cost more than the best pyrites.

(2) *Sulphuretted hydrogen from gypsum.*—Cary-Mantrand (*l. c.*) decomposes a mixture of gypsum and coal at a red-heat by HCl gas, whereby $CaCl_2$, CO, H_2S, and S are formed.

Köhsel (Wagner's Jahresb. 1856, p. 57) decomposes gypsum reduced by coal (that is, CaS) by carbonic acid, burns the H_2S given off to SO_2, and conveys the latter into lead chambers.

3. *Sulphuric acid direct from gypsum.*—Von Seckendorff (Wagner's Jahresb. 1855, p. 54) decomposes gypsum by lead chloride at 75° C. into $CaCl_2$ and $PbSO_4$. A mixture of the latter salt (5 molecules) with muriatic acid of 33° Tw. (4 molecules) at 75° C.

operation) and sulphuric acid (which is decanted and concentrated, the distilling HCl being condensed).

Shanks has patented Seckendorff's process for England (Oct. 9th, 1854).

Margueritte (patent of Dec. 22, 1854) decomposes lead phosphate by muriatic acid; hereby $PbCl_2$ and phosphoric acid are formed; the latter, ignited with gypsum, yields calcium phosphate and sulphuric anhydride. The calcium phosphate and lead chloride, boiled together, regenerate lead phosphate, along with $CaCl_2$, which is worthless; so that the muriatic acid is always lost.

From Lead Sulphate.

Keller (Wagner's Jahresb. 1859, p. 138) decomposes lead sulphate, disintegrated in water, by H_2S into PbS and sulphuric acid; by calcining the PbS it is reconverted into $PbSO_4$. This is, properly speaking, a proposal for utilizing sulphuretted hydrogen.

IV. *Utilization of Sulphuretted Hydrogen for manufacturing Sulphuric Acid.*

To this category belong several of the above-mentioned proposals (Kuhlmann's, Cary-Mantrand's, Köhsel's, Keller's, &c.). But, apart from these, nearly all proposals for making soda by sodium sulphide, and several others, are founded upon this. They will be described in the Chapter on that subject, as they never appear as independent processes for manufacturing sulphuric acid; here it will be sufficient to mention that none of them has accomplished its purpose, as the direct combustion of sulphuretted hydrogen yields too poor a gas.

V. *Calcining Pyrites with salt.*

Kenyon and Swindells (English patent, May 21st, 1872) calcine the chlorides of sodium or potassium with iron- or copper-pyrites, and treat the gas with nitric or chromic (!) acid in high towers, in order to convert the sulphurous into sulphuric acid; at the same time chlorine is given off. Wagner (Jahresb. 1874, p. 272) points out that in this process the sulphuric acid must remain behind in alkaline sulphates.

VI. *By Electricity.*

Reynoso, in 1875, obtained a patent for causing electric sparks to pass through a compressed and cooled mixture of sulphurous acid and atmospheric air. The formation of SO_3 from a mixture of 2 vols. SO_2 and 1 vol. O by the electric spark was first observed in 1860, by H. Buff and A. W. Hofmann (Ann. Chem. Pharm. cxiii. p. 129); Deville (Bull. Soc. Chem. [2] iii. p. 366) has observed that in the presence of strong vitriol, which absorbs the SO_3, the whole gaseous mixture can be united to form SO_3 in this way.

CHAPTER XIX.

APPLICATIONS OF SULPHURIC ACID, AND STATISTICS.

The *principal applications* of sulphuric acid are the following:—

I. In a more or less *dilute* state (say from 144° Tw. downwards). Above all, for making sulphate of soda (saltcake) and muriatic acid, and therefore ultimately for soda-ash, bleaching-powder, soap, glass, and innumerable other products. Further, of superphosphates and other artificial manures. (According to an estimate, made by Dr. R. A. Smith, in 1876, there were used in England 160,000 tons of sulphur for alkali and 100,000 tons for manures, both in the shape of pyrites.) These two applications probably consume nine tenths of all the sulphuric acid produced. Further applications are:—for preparing sulphurous, nitric, phosphoric, hydrofluoric, boric, carbonic, chromic, oxalic, tartaric, citric, acetic, and stearic acids; in preparing phosphorus, iodine, bromine, the sulphates of potassium, ammonium, barium (*blanc fixe*), calcium (*pearl hardening*); especially also for precipitating baryta or lime as sulphates in chemical processes; sulphates of magnesium, aluminium, iron, zinc, copper, mercury (as intermediate stage for calomel and corrosive sublimate); in the metallurgy of copper, cobalt, nickel, platinum, silver; for cleaning (pickling) sheet iron to be tinned or galvanized; for cleaning copper, silver, &c.; for manufacturing potassium bichromate; for working galvanic cells, such as are used in telegraphy, in electro-plating, &c.; for manufacturing ordinary ether and the composite ethers; for manufacturing garancine; for making or purifying many organic colouring-matters, especially in the oxidizing mixture of potassium bichro-

mate and sulphuric acid ; for parchment paper ; fo
mineral oils, and sometimes coal-gas ; for manu
sirup, and sugar ; for the saccharification of corn ;
the alkaline reaction of fermenting liquors, such
effervescent drinks ; for preparing tallow previous
for recovering the fatty acids from soap-suds ; for
table fibres in mixed fabrics ; generally, in dyeing
tanning, as a chemical reagent in innumerable cas
against lead poisoning, and in many other cases.

II. *In a concentrated state* (as *commercial* 1
manufacturing the fatty acids by distillation ; pu
manufacturing pyroxyline, nitrobenzene, picric
nitro-compounds or nitric ethers ; for purifying
leum, paraffine oil, and other mineral oils ; for m
the method of Deville and Debray ; for drying
laboratory purposes, but also for drying chlorine
cess (for this, weaker acid also, of 140° Tw., can b
sally, as a means for attracting water.

III. *In the most concentrated state* (as *real*
refining gold and silver, desilvering copper, &
organo-sulphonic acids ; dissolving indigo ; prepa
compounds and nitric ethers, especially in manu
glycerine.

IV. *As fuming oil of vitriol.* For dissolving in
facturing certain organo-sulphonic acids (in the
alizarine, eosine, &c.) ; for purifying ozokerite ; 1
blacking.

According to Post (Grundr. d. chem. Technol.
make of sulphuric acid in 1875 amounted to 882
lated as 170° Tw.) ; of this, Great Britain supplied
$\frac{1}{6}$, Germany $\frac{1}{8}$, Austro-Hungary $\frac{1}{20}$, Belgium $\frac{1}{30}$.
not mentioned here, produces a somewhat conside
vitriol.) This agrees very nearly with Lamy's
same year.

According to Roscoe and Schorlemmer (Le

1877, i. p. 216), the make in Great Britain alone amounted to upwards of 16,000 tons per week (including all the acid used for alkali &c.).

The production of sulphuric acid in France amounted in 1867 to 90,000 tons, in 1877 to 150,000 tons (Official Exhibition Report).

Prussia in 1874 (Wagner's Jahresbericht, 1876, p. 329) produced 41756 tons of "metallurgical sulphuric acid" (including all made from pyrites, not from brimstone); the total production of Prussia in 1876 (Zeitsch. f. d. Chem. Grossgew. i. p. 70) amounted to 69,985 tons acid of 170° Tw., in 19 factories, with 836 men, at the value of £271,860. One tenth of the raw material consisted of metallurgical intermediate products. (This is only the acid made for sale, and exclusive of that used up at the same works for alkali, manure, &c.)

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